

Scanning Transitiometry

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1 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, when the second is kept constant. This procedure allows direct measurements of the most important thermodynamic derivatives.¹ Temperature-controlled scanning calorimeters (TCSC), in which temperature is taken as the inducing variable and varied as a linear² or stepwise³ 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 program, so that the thermodynamic significance of the calorimetric output signal is not clear. Pressure-controlled scanning calorimeters (PCSC) in which pressure is the inducing variable and is varied as a linear^{4–6} or stepwise function of time^{7–9} are examples of isothermal scanning calorimeters allowing measurements of $(\partial S/\partial p)_T$. Calibration of the pump piston displacement as a measure of the volume change inside the cell⁹ 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 procedures become more difficult to attain in this case, because volume is an extensive parameter.

The three techniques all involve closed systems; any change in the composition results from perturbation of the thermodynamic state by a variation of the inducing independent variable. The possibility of controlling the three most important thermodynamic variables (p, V, T) in calorimetric measurements makes it possible to realize simultaneous measurements of changes or rates of such changes of both thermal and mechanical contributions to the thermodynamic potential change caused by the perturbation. For example, simultaneous recording of both heat flow and volume changes resulting from a given pressure change under isothermal conditions (PCSC) leads to simultaneous determination of both $(\partial S/\partial p)_T$ and $(\partial V/\partial p)_T$ (or isobaric thermal expansivity and isothermal compressibility) as a function of pressure at a given temperature. In the case of the perturbation of the system by a temperature change under isobaric conditions (TCSC), the simultaneous recording of both the

heat flow and volume changes used to keep the pressure constant leads to the simultaneous determination of both C_p and $(\partial V/\partial T)_p$ as a function of temperature at a given pressure. The simultaneous determination of both thermal and mechanical contributions to the total change of thermodynamic potential not only leads to the complete thermodynamic description of the system under study, but also permits investigation of systems with limited stability or systems with irreversible transitions. This approach is also very useful in analysing the course of a transition. By a proper external change of the controlling variable the transition under investigation can be accelerated, impeded or even stopped at any degree of its advancement and then taken back to the beginning, all with simultaneous recording of the heat and mechanical variable variations.¹⁰ This permits not only determination of the total changes of the thermodynamic functions for the transition but also allows analysis of their evolution along the advancement of the transformation. The technique described in this review is called transitiometry, from latin transitio – change, and greek $\mu\epsilon\tau\rho\omicron\nu$ – measure, because it permits direct investigation of physicochemical transitions of various types and a much deeper description than could be done with separate calorimetric and/or dilatometric analysis.

The aim of this review is to present the thermodynamic foundations of the technique, describe typical instrumentation, experimental procedures and software, as well as to exemplify its use with some recent applications.

2 Thermodynamic Foundations

For simplicity the thermodynamic formulae given in this paragraph are written for one mole of a pure substance. The enthalpy differential is described by eqns. (1) and (2).

$$dh(T,p) = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \quad (1)$$

$$dh(T,p) = dQ + vdp \quad (2)$$

When the pressure is kept constant and the temperature is varied as a linear function of time, see eqn. (3).

$$dp = 0, \quad T = T_0 + bt, \quad dT = bdt \quad (3)$$

Eqns. (1) and (2) reduce to eqn. (4).

$$\frac{dQ}{dt} \Big|_p = q_p(T) = \left(\frac{\partial h}{\partial T}\right)_p b \quad (4)$$

where $q_p(T)$ is the power generated or absorbed under isobaric conditions and b is the rate of linear temperature variation. This is the fundamental thermodynamic principle for temperature-controlled scanning calorimetry (TCSC) at constant pressure.²

When the temperature is kept constant and the pressure is varied as a linear function of time, see eqn (5).

$$dT = 0, \quad p = p_0 + at, \quad dp = adt \quad (5)$$

Eqns. (1) and (2) reduce to eqn. (6).

$$\frac{dQ}{dt} \Big|_T = q_T(p) = \left[\left(\frac{\partial h}{\partial p}\right)_T - v \right] a = \left(\frac{\partial s}{\partial p}\right)_T Ta - \left(\frac{\partial v}{\partial T}\right)_T Ta \quad (6)$$

where $q_T(p)$ is the power generated or absorbed under isothermal conditions and a is the rate of pressure variation. This is the funda-

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mental principle for pressure-controlled scanning calorimetry (PCSC)^{4,5}

To introduce volume as an independent thermodynamic variable it is advantageous to write thermodynamic equations (7) and (8) for the change of internal energy

$$du(T,V) = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV \quad (7)$$

and

$$du(T,V) = dQ - pdV \quad (8)$$

When the volume is kept constant and the temperature is varied as a linear function of time, see eqn (9)

$$dV = 0, \quad T = T_0 + bt, \quad dT = bdt \quad (9)$$

Eqns (7) and (8) reduce to eqn (10)

$$\frac{dQ}{dt} \Big|_V = q_V(T) = \left(\frac{\partial u}{\partial T}\right)_V b \quad (10)$$

where $q_V(T)$ is the power generated or absorbed under isochoric conditions. This is the fundamental principle for temperature-controlled scanning calorimetry (TCSC) at constant volume.

When the temperature is kept constant and the volume is varied as a linear function of time, see eqn (11)

$$dT = 0, \quad V = V_0 + ct, \quad dV = cdt \quad (11)$$

Eqns (7) and (8) reduce to eqn (12)

$$\frac{dQ}{dt} \Big|_T = q_T(V) = \left[\left(\frac{\partial u}{\partial V}\right)_T + p\right]c = \left(\frac{\partial s}{\partial V}\right)_T cT = -\left(\frac{\partial p}{\partial T}\right)_V cT \quad (12)$$

where $q_T(V)$ is the power generated or adsorbed under isothermal conditions and c is the rate of linear volume variation. Eqn (12) is the fundamental principle for a technique which, similarly, is called volume-controlled scanning calorimetry (VCSC) at constant temperature.

In all the cases presented above of two independent thermodynamic variables of a system under investigation, one is always kept constant and the other is controlled in a well-defined manner (linear variation). The resulting output signal of such a process is the rate of heat exchange (thermal power of the process) measured by the calorimetric detector. Thus, one can see that calorimetry, when properly used, is a powerful technique which enables the full thermodynamic description of a substance under investigation by measurements of its thermodynamic derivatives. For example, when the substance under investigation is an ideal gas, the derived equations reduce to

(a) pressure-controlled scanning calorimetry (PCSC) at constant temperature, eqn (13)

$$p = at, \quad q_T(p) = -Ta \left(\frac{\partial v}{\partial T}\right)_p = -av \quad (13)$$

(b) volume-controlled scanning calorimetry (VCSC) at constant temperature, eqn (14)

$$V = ct, \quad q_T(V) = -Tc \left(\frac{\partial p}{\partial T}\right)_V = -cp \quad (14)$$

(c) temperature-controlled scanning calorimetry (TCSC) at constant pressure, eqn (15)

$$T = bt, \quad q_p(T) = b \left(\frac{\partial h}{\partial T}\right)_p = bT \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_s = vb \left(\frac{\partial p}{\partial T}\right)_s \quad (15)$$

(d) temperature-controlled scanning calorimetry (TCSC) at constant volume, eqn (16)

$$T = bt, \quad q_V(T) = b \left(\frac{\partial u}{\partial T}\right)_V = bT \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial v}{\partial T}\right)_s = pb \left(\frac{\partial v}{\partial T}\right)_s \quad (16)$$

Relations (13)–(16) not only directly confirm the possibilities of scanning calorimetry and prove the accuracy of the presented definitions, but can also be applied for calibration and/or verification of

given calorimetric systems with the use of ideal gases or of gases for which the thermodynamic properties are known. The above relations also show that by properly combining the scanning calorimetric measurements on the same substance it is possible also to determine isentropic derivatives. For example, eqns (13) and (15) show that combining scanning calorimeters controlled by pressure and temperature makes it possible to determine the isentropic temperature coefficient of pressure, eqn (17)

$$\left(\frac{\partial p}{\partial T}\right)_s = -\frac{aq_p(T)}{bq_T(p)} \quad (17)$$

All the above relations have been derived for linear variations of the inducing variables. Of course, other continuous functions could be used, but the constants a , b and c would then have to be replaced by the time derivatives of these functions. The rates a , b and c should be introduced into the derived equations together with their signs, “–” for decreasing and “+” for increasing direction. It is also possible to use stepwise variations of the inducing variables, but the thermal power of the process must be replaced by the amount of heat exchanged due to this inducing stepwise change.

Applying the principle of equality of the second crossed derivatives pressure derivatives could be determined (for example the isothermal compressibility κ_T) from a set of data on the temperature derivatives, from measurements of the isobaric thermal expansivity α_p obtained with the PCSC technique over large pressure and temperature ranges, eqn (18)

$$\frac{\partial^2 v}{\partial p \partial T} = \frac{\partial^2 v}{\partial T \partial p} \leftrightarrow \frac{\partial \alpha_p}{\partial p} = -\frac{\partial \kappa_T}{\partial T} \quad (18)$$

However, such a procedure involving differentiation of experimental data can cause a loss of precision in the derived thermodynamic description of the process under investigation. Thus, it is advantageous to directly measure the variations of the non-controlled (dependent) mechanical variable simultaneously with the calorimetric signal. The next section presents an instrument which allows determination of the derivative of the recorded variable with respect to the scanned variable simultaneously with the measurement of the thermal effect of the transformation under investigation. Such a procedure not only increases the precision of the method and speeds up the measurements, but also is very advantageous in investigating materials and processes with irreversible transitions, thermal or mechanical instabilities.

3 Instrumental

3.1 General

The fundamental thermodynamic principles presented above can be realized on a number of ways in a moderately equipped physico-chemical laboratory. This chapter presents practical information based on the experience of the author in constructing a number of instruments of this type. However, the technical details and diagrams presented below have been taken from the actual version of the instrument that has been patented and commercialized^{10,11}. All four thermodynamic situations derived above together with recording of the variations of the dependent mechanical variable have been realized in one computer controlled instrument¹⁰. The organization of the instrument software is presented in Fig. 1.

Each of the four logical elements of the digital control system is responsible for the realization of one of the four thermodynamic situations. Of two independent variables (the upper pairs in the block presentation in Fig. 1), one is always kept constant and the other is programmed as a given function of time. The output signals (the lower pairs in the block presentation in Fig. 1) are always heat and variations of the dependent mechanical variable (pressure or volume). The volume variations are recorded by counting the number of motor steps of the stepping motor driving the piston of the high-pressure pump. A general block diagram of a commercial instrument of this type¹¹ is presented in Fig. 2. The calorimetric vessels placed in the calorimetric detector are connected to the high-pressure pump with stainless-steel capillaries. The piston of the

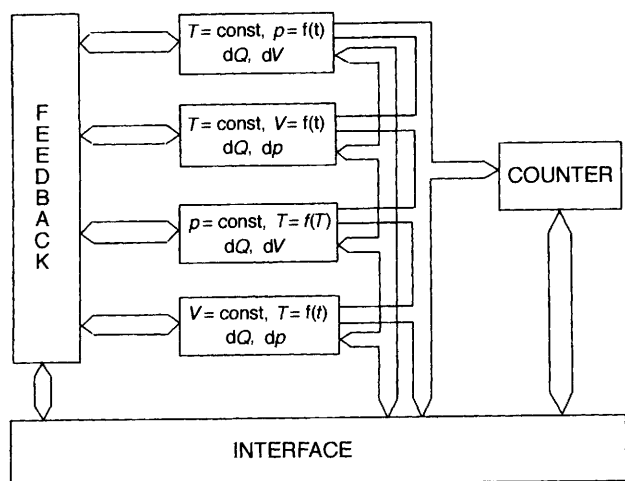


Figure 1 Schematic diagram of the software organization of a transiometer^{10,11}

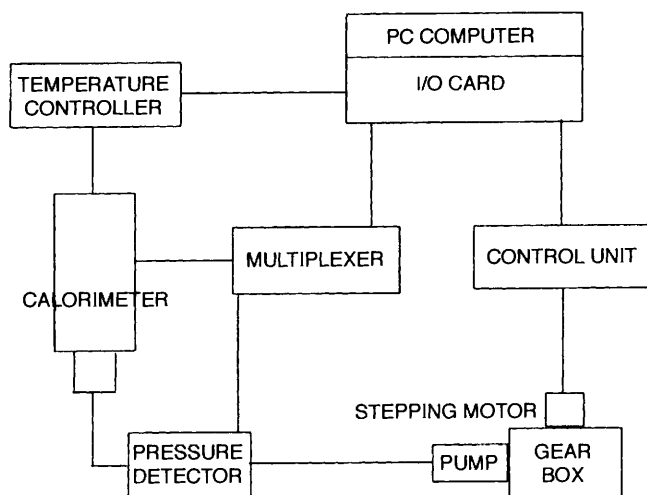


Figure 2 A schematic block diagram of a transiometer¹¹

pump is driven by a stepping motor through a gear box. The stepping motor is connected to the computer interface through a control unit with sufficient power to drive the pump up to 400 MPa. No power is dissipated when the stepping motor is at rest.¹² The output signals from both the calorimetric and pressure detectors are connected to the computer interface through a multiplexer. The temperature controller is directly connected to the computer interface. The temperature range of the actual instrument is 213 to 503 K. The total volume of the sample can be varied from 0.5 to 2.5 cm³, depending on the kind of measurement performed. Typical scanning rates are $T: 8 \times 10^{-4} \text{ K s}^{-1}$, $V: 2 \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$, and $p: 2 \text{ kPa s}^{-1}$. These low rates allow measurement near equilibrium for many processes. Once the sample is loaded into the experimental vessel, the phenomenon under investigation can be observed in various thermodynamic planes.

3.2 Programming and Recording of Mechanical Variables

One of the basic conditions that must be fulfilled to make transiometry an accurate method of investigation is the programming of the given inducing variable as a strictly linear function of time (or any other function), independent of internal and external disturbances. The propagation of the inducing variable variations must also be homogeneous over the whole sample under investigation. Any disturbance of the homogeneity or linearity of the inducing variations will cause perturbations of the output signals and the relations derived will not be valid.

The measurement, control and programming of temperature vari-

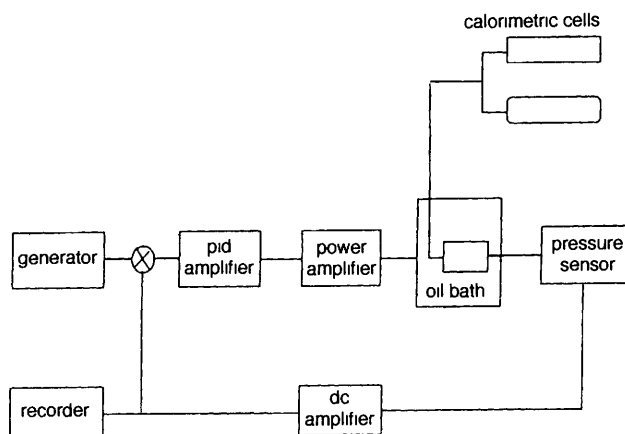


Figure 3 A block diagram of a thermally controlled pressure programmer¹

able have often been discussed in the literature and a description is omitted here. But, the description of programming of mechanical variables has been limited to a few specialized periodicals,^{4,13,14} and a short description of related problems will be presented here. One of the simplest methods of generation, control and programming of pressure in thermodynamic investigations is heating or cooling an external tank connected hydraulically with experimental vessels and a pressure detector. A schematic block diagram of such a pressure programming system is presented in Fig. 3. An external tank connected to the calorimetric vessels and to the extensimetric pressure detector through stainless steel capillaries is placed in an oil bath. The heating or cooling of the oil bath depends on the difference between the signal coming from the pressure detector and from the signal generator. The desired function of time for the pressure in the system is chosen by setting the signal generator to produce such a signal. The amplitude of such a signal must be normalized with the signal coming from the pressure detector. The difference of these two signals is then corrected by a PID amplifier which drives the power amplifier connected to the heater of the oil bath. If the difference is close to zero, the pressure in the system is nearly equal to the pressure resulting from the actual value of the set function supplied by the signal generator. A detailed analysis of such a system is given elsewhere.^{4,5} If the signal generator is set to produce a given constant value, then the pressure in the system will remain constant independent of the internal changes in the calorimetric system. For example, the calorimetric vessels can be heated under constant pressure. If a separating ring is placed in the tubing of a known diameter connecting the external tank and the calorimetric vessels, then recording the position of the ring measures the compensating volume changes used to keep the pressure constant.¹⁴ Unfortunately, this simple technique only gives satisfactory results up to about 100 MPa. For higher pressures it is much better to use a piston pump driven by a stepping motor and a gear box.^{6,9-13} The stepping motor can easily be controlled by frequencies generated in a computer. The connection of the stepping motor to the computer must be done by an interface with sufficient power to drive the pump.

Computer control of the stepping motor gives practically unlimited possibilities of creating software for controlling, programming and recording of both pressure and volume variations. The volume variations can be performed and measured by proper calibration of the motor steps. The volume calibration of the motor steps can be done by several techniques: (i) a simple weighing of a liquid of a known density pushed away from the system by moving the pump piston with a given number of motor steps, (ii) by compressing or/and decompressing a liquid with known compressibility,^{9,15} (iii) by isobaric compensation for the volume change in a phase transition with a known volume change,¹⁰ etc. After the motor steps have been calibrated as volume variations, volume changes due to the compressibility of the hydraulic fluid present in the system must be determined. This can be done by compressing and/or decompressing with only the hydraulic liquid

present in the system. The reproducibility of such measurements is a few tenths of a percent over large pressure and temperature ranges.⁹

One of the important problems is attainment of the inducing variables as given functions of time without transient overshoots. In the classic analogue electronic control this can be done by a proper adjustment of PID parameters of the controller/programmer.^{4,16} In digital control, especially in the case of pressure programming it is possible to use a complex control variable which when transformed into frequencies drives the stepping motor.^{12,13,15} In the instrument schematically presented in Fig. 2 the control variable (CV) is composed of two parts, $CV = PR + COR$. PR is a constant proportional to the chosen speed of pressure variations, and COR is a dynamic correction obtained using the control function (CF). PR is determined at the beginning of the program from the limiting speed characteristic (LSC) of the controlled system. LSC gives maximal rates of pressure variations which correspond to the maximal frequencies which can be used as a function of pressure. LSC is determined once in a separate calibration experiment and loaded in a logical element of the programming system. The control function can be a digital equivalent to P, PI or PID and has as argument the difference between the actual pressure in the system and the value resulting from the set function. A schematic block presentation of such a digital programming loop is given in Fig. 4. The program starts with the control variable equal to PR determined from LSC on the basis of a simple proportionality between the maximal admissible rate of pressure variations at the actual start pressure and the speed of pressure variations set for the actual scanning. This initial value of PR is transformed into frequency and sent through the interface to the stepping motor. Any change in the compressibility of the system which causes a pressure deviation from the set function (SF) is detected by the correction term COR, which is varied by the negative feedback in such a manner as to compensate for internal volume changes and to reach the pressure set function without disturbances.

The procedures described above can give good results even when programming with very low rates over large pressure ranges. However, one of the important conditions which must be fulfilled is a high resolution of the pressure detector. When using an extensometric pressure detector with five digit resolution, pressure programming with a rate as low as 2 kPa s^{-1} over the pressure interval of 400 MPa can be performed with simultaneous recording of the volume variations.¹¹

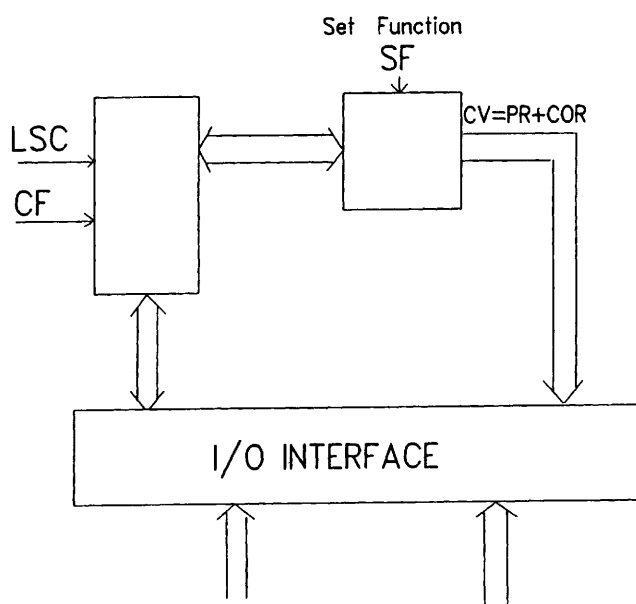


Figure 4 A schematic diagram of an element of the control loop for digital pressure programming. Symbols are defined in the text.

3.3 Calorimetric Measurements of Thermal Power

The thermodynamic foundations of scanning transitiometry [eqns (1–18)] require that the calorimetric signal represents the thermal power developed under given conditions. Unfortunately, most calorimeters that can be used do not measure power directly, but rather a temperature or temperature difference recorded as a thermogram. The power developed by the process in the experimental vessel is distributed and accumulated inside the calorimetric cell and exchanged with the environment. This means that the recorded thermogram is defined by the balance of power in the calorimeter and not by the power itself. Because the balance of power is not independent of the calorimetric system, the recorded thermogram depends not only on the process under investigation but also on the calorimetric detector used. A presentation and analysis of techniques used to correct the calorimetric thermograms in order to get the thermal power have already been analysed and discussed in review papers^{17,18} and will not be described in detail here. However, some general remarks are presented here as a reminder of the conditions under which such corrections are practically not necessary and can be omitted.

The general equation relating the thermal power $q(t)$ developed in the calorimetric vessel and the recorded calorimetric thermogram $\theta(t)$ can be written in the following form,^{19,20} eqn (19)

$$q(t) = \frac{1}{\sum a_i \tau_i} \left[\theta(t) + \sum \tau_i \frac{d\theta(t)}{dt} + \sum_{i \neq j} \tau_i \tau_j \frac{d^2\theta(t)}{dt^2} - \sum_{i \neq j \neq k} \tau_i \tau_j \tau_k \frac{d^3\theta(t)}{dt^3} + \tau_i \tau_j \tau_k \tau_l \frac{d^4\theta(t)}{dt^4} \right] \quad (19)$$

where $i = 1, 2, \dots, n$ and $i < j < \dots < n$, and τ_i, τ_j, τ_k are time constants of the calorimeter and a_i are coefficients depending on the configuration of the heat exchange in the calorimeter. In the case of a calorimeter with only one time constant eqn (19) is reduced to eqn (20)

$$q(t) = \alpha \left[\theta(t) + \tau \frac{d\theta(t)}{dt} \right] \quad (20)$$

where the time constant is defined as a ratio $\tau = C/\alpha$, with C denoting the heat capacity of the calorimeter and α its static coefficient of heat exchange with the nearest environment. From eqns (19,20) one can see that the thermal power $q(t)$ is directly proportional to the recorded thermogram $\theta(t)$ if the dynamic corrections coming from the contributions containing time derivatives of the calorimetric signal are small. Such a situation can always be achieved if the rate of scanning of the inducing variable is very low and the system under investigation is close to thermodynamic equilibrium. In case of doubt it is always possible to make a check by assuming that the calorimeter is a one time constant system, calculating the contribution from the first derivative term along the thermogram, and comparing it with the actual values of the thermogram itself.

3.4 Experimental Vessels

The equations presented in the introduction are concerned with all elements subject to the variations of the inducing variable in the active field of the calorimetric detector. Thus, it is important to subtract nonsample effects from the total calorimetric output signal and thus obtain the net contribution related only to the phenomenon developed in the substance under investigation. The discussion of such procedures with temperature as inducing variable is well presented in the literature (e.g. refs. 2, 25, 29) and will not be discussed here. However, a few remarks are given concerning the use of pressure as inducing variable. Fig. 5 presents two model situations. In Fig. 5(a) the action of pressure on the substance under investigation is exerted through a hydraulic liquid which occupies a part of the experimental vessel of internal volume V_{in} . In cases where the hydraulic liquid is neutral, like mercury with most non-electrolytes, the sample can be placed directly in the hydraulic liquid. Otherwise, it should be placed in a protective ampoule made of a soft substance to transmit pressure. In Fig. 5(b) pressure is transmitted through the substance itself. In this case, the internal volume V_{in} is filled completely with the investigated substance and in the course of the variation of pressure the mass of the substance will change by an

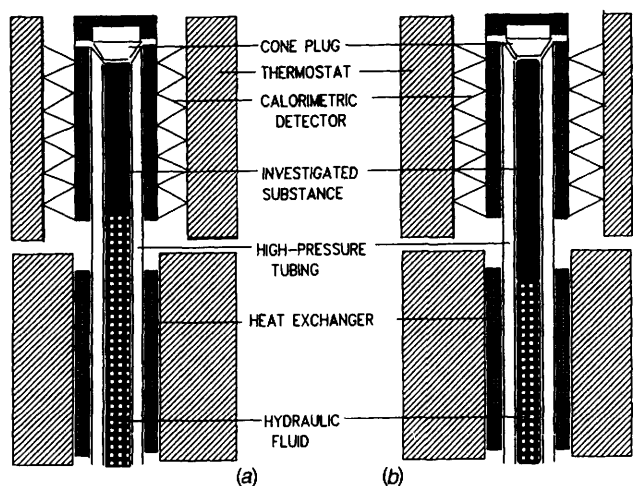


Figure 5 A schematic diagram of high pressure experimental vessels (a) sample constant mass mode, (b) sample constant volume mode

amount equal to the ratio of the internal volume of the vessel to the molar volume of the investigated substance, V_{in}/v_s . In the situation presented in Fig 5(a) the mass of the investigated substance remains constant in the course of the experiment. Thus, the thermal contribution from the substance to the calorimetric output signal [see eqn (6)] is defined by eqn (21)

$$q_T(p) = n_s aT \left(\frac{\partial s_s}{\partial p} \right)_T = -n_s aT \left(\frac{\partial v_s}{\partial T} \right)_p \quad (21)$$

where n_s and s_s represent the number of moles and the molar entropy of the substance under investigation. In the case of the constant sample volume experiment [Fig 5(b)], the calorimetric output signal is defined by eqn (22)

$$q_T(p) = \frac{V_{in}}{v_s} aT \left(\frac{\partial s_s}{\partial p} \right)_T = -aT \frac{1}{v_s} \left(\frac{\partial v_s}{\partial T} \right)_p = (-V_{in} aT \alpha_{p,s}) \quad (22)$$

where $\alpha_{p,s}$ is the isobaric coefficient of thermal expansion of the substance under investigation.

Another problem is the contribution from the experimental vessel itself. When pressure is applied inside a cylinder of internal volume V_{in} it will expand and the volume of the wall of the cylinder, V_w , will increase by an amount which can be approximated by eqn (23)^{21,22}

$$(dV_w)_T = V_w \kappa_{T,w} dp \quad (23)$$

where $\kappa_{T,w}$ is the isothermal coefficient of compressibility of the material from which the cylinder is made. From the Maxwell relation [eqn (24)]

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (24)$$

the thermal effect, eqn (25), is obtained

$$dQ_w = \frac{\alpha_{p,w}}{\kappa_{T,w}} T dV_w \quad (25)$$

When a cylinder is pressurized on the inside, the thermal effect from expansion of the wall is endothermic while a similar thermal effect in the compressed substance [eqn (22)] placed inside is exothermic. Introducing eqn (23) into eqn (25) and using a linear pressure scan eqn (26) is obtained which describes the thermal power developed in the wall of the experimental vessel

$$q_{T,w}(p) = V_{in} aT \alpha_{p,w} \quad (26)$$

Experimental vessels for use over large ranges of pressure and temperature that are also chemically inert are usually made of stainless steel. The thermal expansion coefficient, $\alpha_{p,w}$, for stainless steel ($5.1 \times 10^{-5} \text{ K}^{-1}$)²³ is small with respect to the thermal expansion coefficient of most liquids and transitions studied, and usually can

be taken as independent of both temperature and pressure. Thus, the magnitude of the thermal contribution from the wall of the vessel depends mainly on its internal volume V_{in} . The internal volume can be conveniently determined by filling the vessel with a fluid of known α_p . One such liquid is hexane for which α_p is known over large pressure and temperature ranges²⁴. Such calibration can also be performed with an ideal gas for which $\alpha = 1/T$. The internal volume determined by this procedure is the volume 'seen' by the calorimetric detector. If the vessel and the calorimetric detector are properly designed, this value is nearly equal (to a fraction of a percent⁷) to the mechanical volume resulting from the actual dimensions of both the tubing and calorimetric detector used. Sometimes the internal volume can be conveniently determined simultaneously with the static calibration of the calorimeter and the calibrations expressed as one combined calibration constant⁹.

Thus, the analysis of the calorimetric signal is done with the use of eqns 21 or 22, and 26. The simplest situation is the case of constant sample volume (Fig 5b), where measured thermal power $q_T(p)$ [eqn (27)] is determined per unit volume

$$q_T(p) = -V_{in} aT (\alpha_s - \alpha_w) \quad (27)$$

Eqn 27 shows that thermal power is directly proportional to the difference in the isobaric coefficients of thermal expansion of the substance under investigation and of the material from which the experimental vessel is made. In the case of constant mass measurements [Fig 5(a)] the thermal power $q_T(p)$ is given by eqn (28)

$$q_T(p) = n_s aT \left(\frac{\partial s_s}{\partial p} \right)_T + V_{in} aT \alpha_w - (V_{in} - V_s) aT \alpha_h \quad (28)$$

where V_s is the volume of the sample under investigation and α_h is the thermal expansion coefficient of the hydraulic fluid. If liquid with a low thermal expansivity, such as mercury, is used as hydraulic fluid, then the last contribution in eqn (28) is negligible. In some situations the thermal contributions from both the hydraulic fluid and the wall of the experimental vessel can be compensated by differential mounting of the vessels. Such a situation was analysed in ref 5.

The experimental vessels presented schematically in Fig 5 can be conveniently opened and closed with the help of a torque wrench and a special stand to hold them in place.¹¹ Such a procedure facilitates filling of the vessels and assures their long life and reproducible use even at very high pressure.

4 Studies of Phase Transitions

4.1 General

To discuss interpretation of thermograms recorded during phase transitions the fusion process will be assumed to be a simple, zero order kinetic process. It is well known that transitions from liquid to solid can very easily go through metastable states and can be very far from equilibrium. Control of such processes is very difficult, because once in a metastable state such systems go towards equilibrium at a rate dependent on how far the system is from equilibrium and not dependent on the driving force. On the other hand, transitions from solid to liquid very seldom go through metastable states and their induction can be controlled. When the fusion process starts and the sample is composed of molecules in both liquid and solid states, both crystallization and fusion are controlled by variations of the independent thermodynamic variables. In such a case the entropy of the sample s_s is given by eqn (29)

$$S_s = n_s s_s = n_s s_s(sd) + n_s(lq) [s_s(lq) - s_s(sd)] \quad (29)$$

where $s_s(sd)$ and $s_s(lq)$ stand for the molar entropy of the substance in the solid and liquid states respectively, $n_s(lq)$ is the number of moles of the substance in the liquid state, and n_s is the total number of moles. Surface contributions to the entropy of the sample have been neglected in eqn (29). In the case of an isothermal process differentiation of eqn (29) against pressure at constant temperature gives eqn (30)

$$n_s \left(\frac{\partial s_s}{\partial p} \right)_T = n_s \left[\frac{\partial s_s(sd)}{\partial p} \right]_T + n_s(lq) \left\{ \left[\frac{\partial s_s(lq)}{\partial p} \right]_T - \left[\frac{\partial s_s(sd)}{\partial p} \right]_T \right\} + \left[\frac{\partial n_s(lq)}{\partial p} \right]_T [s_s(lq) - s_s(sd)]. \quad (30)$$

Eqn. (31) is obtained by introducing eqn. (30) into eqn. (28) and neglecting the contributions from the hydraulic liquid and the vessel.

$$q_T(p) = aT \left\{ n_s \left(\frac{\partial s_s(sd)}{\partial p} \right)_T + n_s(lq) \left[\left[\frac{\partial s_s(lq)}{\partial p} \right]_T - \left[\frac{\partial s_s(sd)}{\partial p} \right]_T \right] \right\} + aT \left[\frac{\partial n_s(lq)}{\partial p} \right]_T [s_s(lq) - s_s(sd)]. \quad (31)$$

$$aT \left[\frac{\partial n_s(lq)}{\partial p} \right]_T [s_s(lq) - s_s(sd)] = \left[\frac{\partial n_s(lq)}{\partial t} \right]_T \Delta h_{Fus} = q_{Fus}(p) \quad (32)$$

where Δh_{Fus} is the molar enthalpy of fusion of the substance under investigation. The other terms in eqn. (31) define contributions to the calorimetric signal from both the appearing liquid phase and the disappearing solid phase. The respective magnitudes of those contributions change as a function of the process.

A schematic model diagram of fusion in the transitiometer is presented in Fig. 6.⁵ For simplicity, the analysis is done with the use of linear coordinates. In such a case the power of fusion can be expressed as eqn. (33),

$$q_{Fus} = A\rho l \frac{dx}{dt} \quad (33)$$

where x is the thickness of the liquid layer, ρ is the density of the liquid layer, l is the specific heat of fusion of the substance under investigation and A is the active area of the heat exchange in the experimental vessel.

The thermal power q_1 exchanged through the liquid layer between the calorimetric cell and the liquid–solid interface in the steady state is expressed by eqn. (34).

$$q_1 = \frac{A\lambda(T_c - T_{Fus})}{x} \quad (34)$$

where λ is the heat conductivity of the liquid substance, T_c is the temperature of the calorimetric cell and T_{Fus} is the temperature of fusion of the substance. In this simple geometrical model the area of heat exchange through the liquid layer does not depend on the advancement of fusion.

The power q_{th} exchanged in the steady state between the calorimetric cell and the thermostat is expressed as eqn. (35),

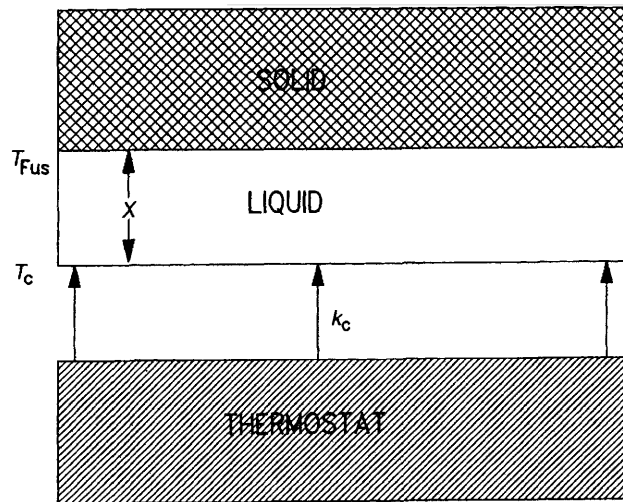


Figure 6 A schematic model diagram of a fusion process in a transitiometer with an assumption of planar geometry of heat exchange

$$q_{th} = k_c (T_T - T_c) \quad (35)$$

where k_c is the static gain of the calorimetric cell¹⁷ and T_T is the temperature of the thermostat. In the steady state the exchanged thermal powers must be equal, $q_T = q_1 = q_{th}$, and eqns. (33–35) can be combined to give eqn. (36).

$$k_c \rho l x \frac{dx}{dt} = A\rho l \frac{dx}{dt} + \lambda k_c (T_{Fus} - T_T) = 0 \quad (36)$$

During a phase transition, pressure and temperature are not independent parameters, and the Clausius–Clapeyron eqn. (37) can be used to describe their mutual dependence

$$T_{Fus} = T_{Fus}(p_0) + \frac{p - p_0}{\left(\frac{dp}{dT} \right)_{T_{Fus}(p_0)}}$$

Eqn. (37) is an integrated, series expanded and simplified form of the Clausius–Clapeyron relation. If eqn. (28) is assumed to hold for a given experiment

$$T_T = T_{Fus}(p_0); p_0 = p_{Fus}(T_T), \text{ and } p = p_0 - at \quad (38)$$

one obtains eqn. (39).

$$\frac{\rho l x}{\lambda} \frac{dx}{dt} + \frac{A}{k_c} \rho l \frac{dx}{dt} = \frac{at}{\left(\frac{dp}{dT} \right)_{T_T}}$$

Integration of eqn. (39) gives a relation between time and the thermal power of fusion developed in a calorimeter when the fusion process is controlled by linear pressure variations at constant temperature

$$q_{Fus} = \frac{k_c a}{\left(\frac{dp}{dT} \right)_{T_T}} \left[1 + \frac{k_c^2 a^2 t^2}{A^2 \rho l \lambda \left(\frac{dp}{dT} \right)_{T_T}} \right]^{-\frac{1}{2}} t \quad (40)$$

For small values of time, eqn. (40) has the asymptote eqn. (41), demonstrating that under the defined conditions the thermal power of fusion is a linear function of time

$$q_{Fus} = \frac{k_c a}{\left(\frac{dp}{dT} \right)_{T_T}} t \quad (41)$$

and for large values of time eqn. (42).

$$q_{Fus} = A \left[\frac{\lambda \rho l a}{\left(\frac{dp}{dT} \right)_{T_T}} \right]^{\frac{1}{2}} \quad (42)$$

Notice that the asymptote defined by eqn. (42) is time independent. Such a situation should be avoided when performing measurements. Similar asymptotes for isobaric temperature-controlled fusion are given by eqn. (43) for small values of time

$$q_{p, Fus}(T) = bk_c t \quad (43)$$

$$q_{p, Fus}(T) = A(\lambda \rho l b)^{\frac{1}{2}} \quad (44)$$

Analysis of eqns. (41)–(44) demonstrates that the linear rise of thermal power in the case of temperature inducing is sample independent, depends only on the properties of the instrument (k_c), and on the heating rate applied (b). On the other hand, in the case of pressure inducing, the rate of the linear rise also depends on $(\partial p/\partial T)$ for the transition in the substance under investigation.

The analysis presented above shows that experimental vessels and experiments can be prepared in such a way as to end the fusion in the region of linear rise of thermal power. For example, in the

case of pressure-controlled fusion, the time interval at which the thermal power of fusion increases linearly can be found from relations (40) and (41)

The time interval t_{Fus} in which the differences between the real values of power determined by eqn (40) and the values of power determined by eqn (41) are smaller than one percent, is defined by eqn (45)

$$t_{\text{Fus}} = \frac{A}{k_c} \left[\frac{0.02\rho\lambda l}{a} \left(\frac{dp}{dT} \right)_{T_r} \right]^2 \quad (45)$$

In this time interval only a certain quantity of substance can be fused. This quantity m_{Fus} and its relation with the time interval t_{Fus} can be found from eqn (39) by substituting $m_{\text{Fus}}/A\rho$ for x (see Fig 6) and integrating, eqn (46)

$$t_{\text{Fus}} = \left[\frac{m_{\text{Fus}}}{a} \left(\frac{m_{\text{Fus}}}{\lambda\rho A^2} + \frac{2}{k_c} \right) \left(\frac{dp}{dT} \right)_{T_r} \right]^2 \quad (46)$$

From relations (45) and (46) the mass that will be fused during the linear rise of the thermal power is given by eqn (47)

$$m_{\text{Fus}} = \frac{0.01\rho\lambda A^2}{k_c} \quad (47)$$

If the mass of the sample is greater than the value determined by eqn (47), the thermogram will be linear only up to a certain time, after which it will go in the direction of the time-independent asymptote. The same relation holds for temperature-controlled fusion.

Eqn (31) shows that the contribution from the transition itself is not the only effect influencing the shape of the thermogram. Two other terms related to the thermodynamic derivatives of the investigated substance in both the solid and liquid phases and their respective masses present in the experimental vessel also affect the thermogram, and during the process of fusion the mass of solid phase will diminish and the mass of the liquid phase will increase. All these contributions must be taken into consideration when analysing the shapes of transitiometric thermograms.

4.2 Isobaric Transitions

Examples of phase transitions studied with the technique described in this review will first be illustrated by investigation of a typical first order transition, namely fusion of benzene under various conditions. Further possibilities of scanning transitiometry will be illustrated by investigation of phase transitions in liquid crystals over large pressure and temperature ranges with various inducing variables.

Typical calorimetric investigations of phase transitions are measurements assumed to be at constant pressure.²⁵ However, in classical differential scanning calorimetry (DSC) it is difficult to control pressure over the sample when the temperature is varied. The pressure inside the experimental vessel changes due to the volume change and the shape of the recorded thermogram is affected. In transitiometric measurements the pressure in the measuring system is kept constant by compensating the volume changes with a feedback loop like that shown in Fig 4. There are no changes in the compressibility of the hydraulic liquid and the motor steps are all used to compensate the volume change caused by the transition. From the number of motor steps used for such a compensation the volume changes of the investigated transition can be simultaneously determined. Fig 7 presents the isobaric fusion of 1.1409 g of benzene performed at 78.2 MPa by linearly programming temperature from 299.9 to 309.7 K at a rate of 0.83 mK s⁻¹. Actual temperature programming started at 293.1 K, Fig 7 shows only the transition part of the data. Two output signals were simultaneously recorded: (i) thermal (calorimetric), its integral gives the enthalpy change during fusion, (ii) volumetric, proportional to the volume change during fusion.

The multiplicity and variety of phase transitions shown by liquid crystals make them very interesting for investigations by scanning transitiometry. Fig 8 gives both the output calorimetric signal and the volume variations of isobaric transitions in a liquid crystal *S*-(4-

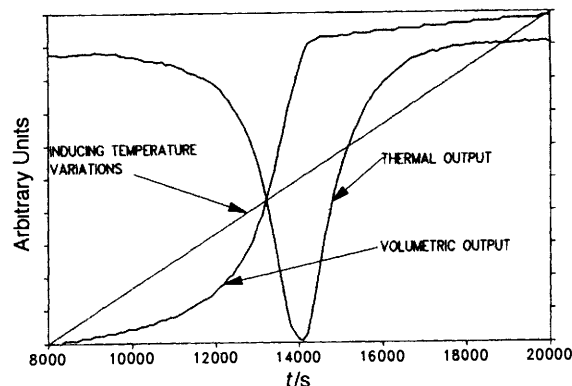


Figure 7 An example of a transitiometric analysis of fusion of benzene under isobaric conditions at 78.2 MPa by a linear temperature increase from 299.9 to 309.7 K at a rate of 0.83 mK s⁻¹.

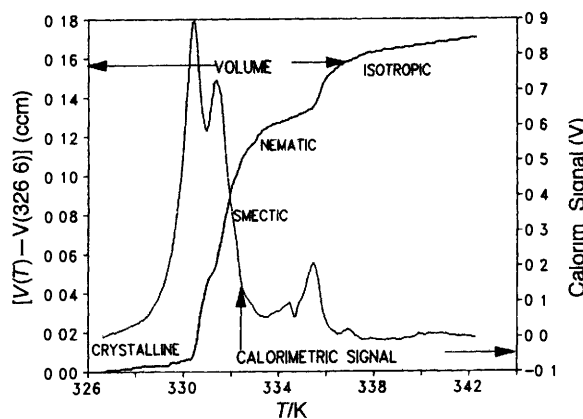


Figure 8 An example of a transitiometric analysis of *S*-(4-pentylphenyl) 4-decyloxythiobenzoate liquid crystal at 80.8 MPa by cooling at a rate of 0.83 mK s⁻¹.

pentylphenyl) 4-decyloxythiobenzoate.²⁶ A sample of the liquid crystal was first pressurized up to 80.8 MPa and heated to reach the isotropic liquid phase at 342.3 K. After thermal and mechanical equilibration of a few hours, a program of linear temperature decrease was started at a rate of -0.83 mK s⁻¹ with simultaneous recording of the calorimetric signal and the volume variations from the number of motor steps needed to keep the pressure constant.

Similar data could probably be obtained by classical DSC by measuring enthalpy changes at various pressures and temperatures and then calculating the volume changes with the Clapeyron equation. However, the error of such a determination is estimated to be about 20%.²⁵ In the actual transitiometer^{10,11} the volume change which corresponds to one motor step is 5.84×10^{-6} cm³. However, such a small volume change has almost no effect on the high-pressure detector and the volume can be compensated only when a change in the pressure in the system is detected. Thus, the practical resolution of the volumetric measurements by this technique depends on the sensitivity of pressure detection. In the actual system used to obtain the results reported in Fig 8 the minimal detectable pressure change caused a volume change of 133 motor steps. Thus, the practical volumetric resolution under isobaric conditions was 8×10^{-4} cm³. The results presented in Fig 8 have the precision of determinations of volume changes from one to four per cent depending on the transition. Such volumetric measurements could be performed with a good high-pressure dilatometer, but this technique has the advantage that the volume variations are recorded simultaneously with the enthalpy changes.

The significance of the data obtained on a transition is increased when isobaric measurements are performed under various pressures. Fig 9 presents results of identical measurements performed with the same sample but at 134.6 MPa. When comparing the results in Figs 8 and 9 not only is there a shift in the temperatures

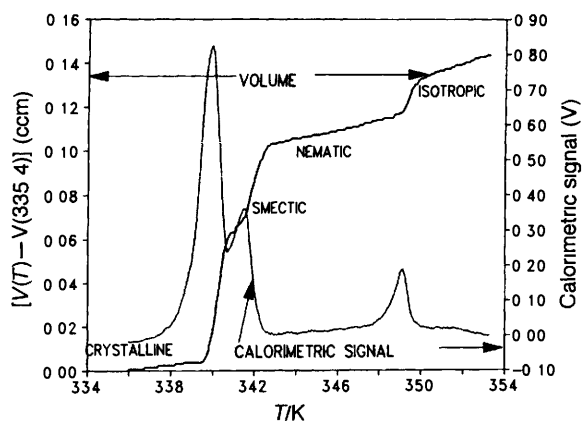


Figure 9 An example of a transitiometric analysis of *S* (4 pentylphenyl) 4 decyloxythiobenzoate liquid crystal by cooling at a rate of 0.83 mK s^{-1} under isobaric conditions at 134.6 MPa

of the transitions, but also a difference in the shapes of the curves, especially in the transition between the crystalline and smectic phases. The isobaric mode of transitiometric analysis can be used only with substances with no risk of their decomposition on heating. When such a risk exists, then it is more advantageous to use the isothermal mode of analysis and gradually increase the temperature of the investigation.

4.3 Isothermal Transitions

Phase transitions can be induced at constant temperature by varying volume or pressure in the system under investigation. So far the isothermal method has not been extensively explored, but, according to the experience of the author the isothermal inducing of phase transitions is especially interesting when investigating the mechanism of transitions. The propagation of the mechanical variable through the investigated substance is much faster than propagation of thermal perturbations. Thus, the dynamic lag in isothermal measurements is very small and often negligible making it possible to stop the transition at any degree of advancement, then to continue or to come back to the beginning and to restart. As an example, the isothermal transitiometric investigation of the fusion of benzene performed under two conditions is presented. Fig. 10 presents data on isothermal solidification. Such transitions from liquid to solid very often go through metastable states. This can be seen in Fig. 10, where the solidification starts at 151 MPa and goes very rapidly to completion (the equilibrium freezing pressure at 303.15 K is 90.2 MPa ²⁷). The process of solidification was so fast that the pressure programming system could not compensate for the internal volume change and a small disturbance is observed on the linear pressure rise in the system. In Fig. 10 the line representing the volume corresponds to the total volume change for both the benzene sample and the hydraulic fluid. The isothermal fusion of benzene performed

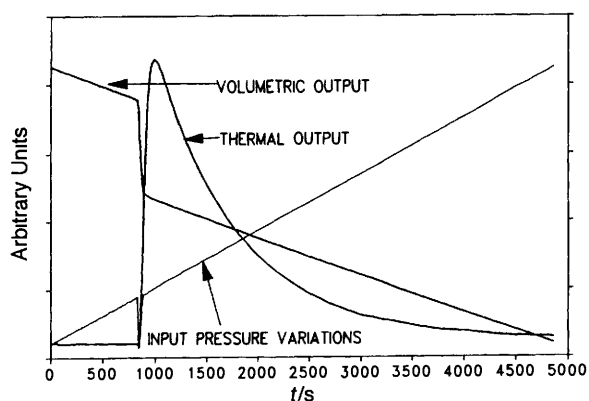


Figure 10 An example of isothermal solidification of benzene at 303.15 K by increasing pressure at a rate of 5 kPa s^{-1}

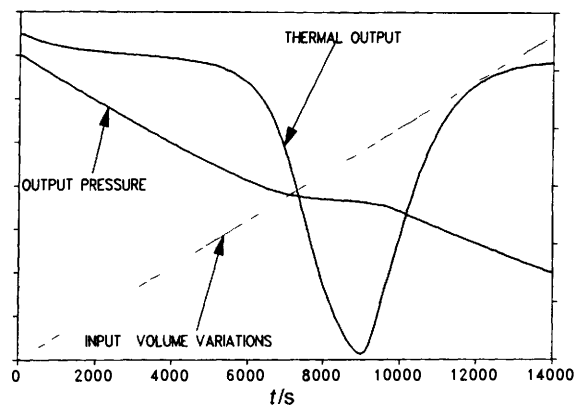


Figure 11 An example of isothermal fusion of benzene at 299.15 K by linear volume change at a rate of $1.17 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1}$

at 299.15 K by increasing the volume of the system at a rate of $1.17 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1}$ is presented in Fig. 11. Under these conditions the pressure in the system was nearly constant and equal to the freezing pressure of benzene (74.6 MPa at 299.15 K)²⁷ during the transition. The isothermal fusion of benzene at 303.15 K performed by a linear pressure decrease at a rate of 5 kPa s^{-1} is presented in Fig. 12. The volume change for fusion was obtained from the number of motor steps used to compensate for the internal volume change and maintain the linear pressure decrease. In Fig. 12 the volume changes for decompression of the hydraulic fluid were subtracted and the volume variations presented correspond to the volume of fusion of benzene. Determination of the volume changes of the hydraulic fluid were performed in a separate experiment where only the hydraulic fluid was present in the system. Contrary to the situation presented in Fig. 10, the process is completely controlled by the linear pressure decrease, because the internal volume changes are completely compensated for by the pressure programming system.

The results presented in Fig. 12 correspond directly to the thermodynamic analysis presented for the fusion process at the beginning of this section, thus it is interesting to compare the thermodynamic model with the experimental results. Both the calorimetric and volumetric outputs have linear portions as it was predicted by the analysis [see eqn. (41)]. However, at the beginning of the transition the situation is not completely clear. It must be remembered that the linear asymptote was derived only for the contribution from the fusion. When analysing the shape of the output signals the complete form of eqn. (31) must be taken into consideration, because the pressure derivatives of the entropies of both solid and liquid phases also contribute to the output signal. It is not completely clear whether this can explain all the effects observed at the beginning of fusion. However, the most interesting observation is that this behaviour is observed on both the calorimetric and volumetric signals. This means that thermal lag is not the main cause of this effect. The thermodynamic analysis of the fusion process was

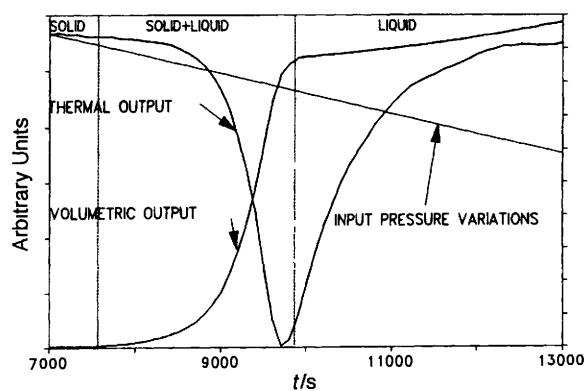


Figure 12 Transitiometric analysis of fusion of benzene at 303.15 K by a linear pressure decrease at a rate of 5 kPa s^{-1}

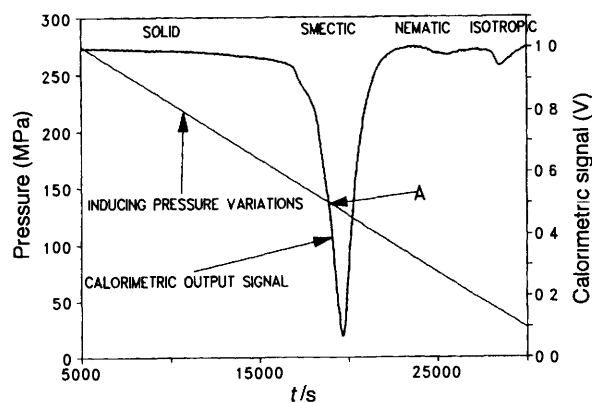


Figure 13 An example of a transitiometric analysis of phase transitions in (4-pentylphenyl) 4-decyloxythiobenzoate liquid crystal by decreasing pressure at a rate of 10 kPa s^{-1} at 370 K

performed in linear coordinates for simplicity, but the experimental results presented are for experiments in a cylindrical vessel. Thus, the internal heat exchange should have a slightly different time dependence of the process because the active area of heat exchange A [see eqns (33) and (34)] changes as a function of the advancement of fusion. Surface tension and surface fusion were also not considered in the analysis. A more advanced analysis of phase transitions under pressure should take into consideration all of these effects. In Fig. 12 the pressure interval of coexistence of phases is rather large compared to the rate of pressure change. This makes it possible to investigate the mechanism of the transition as a function of advancement.

Further results are illustrated by transitions in (4-pentylphenyl) 4-decyloxythiobenzoate liquid crystal. This liquid crystal has three smectic phases, A, B, and C, all observable only on cooling; on heating the solid phase goes directly to the smectic-A phase.²⁸ From thermodynamics a compression of a system corresponds to cooling, and decompression to heating. Fig. 13 presents an example of a decompression at 370 K performed at a rate of 10 kPa s^{-1} . At 370 K under atmospheric pressure this liquid crystal is in the isotropic liquid phase. For simplicity only the calorimetric output signal is given. There is only a small disturbance at the beginning of the transformation and it is rather difficult to distinguish other transitions on the peak for the solid-to-smectic-A transition. However, if pressure programming was stopped at a certain point in the disappearance of the solid phase and the system recompressed, it was possible to observe distinguishable peaks in the output. The distribution of peaks as a function of pressure and their shapes depended strongly on the initial advancement of the transition. Fig. 14 gives three thermograms obtained by recompressions at a rate of 5 kPa s^{-1} starting from various pressures where the transition had previously been stopped (in the vicinity of point A in Fig. 13). On recompression of a system with coexisting phases, passage to the solid phase takes place with distinctive transitions, represented on the output signal by distinguishable peaks. Most probably these peaks correspond to the appearance of the respective smectic phases.

This article is not concerned with elucidation of complicated behaviour of liquid crystals at high densities. Its aim is to demonstrate the new possibilities of scanning transitiometry in such investigations. Scanning transitiometry can be used not only in making phase diagrams, but is also very useful in investigating the mechanism of a transition. The above examples show that the pressure variable is especially interesting for many reasons. The main experimental advantage is easier control of transitions induced by pressure than by temperature due to the fast propagation and larger pressure intervals of coexistence of phases.

The analysis of transitiometric output signals was devoted mainly to the fusion process and examples of results obtained were limited only to various phase transitions. The information given in this review suggests similar investigations can be performed for chemical reactions, transformations in biochemical and biological systems

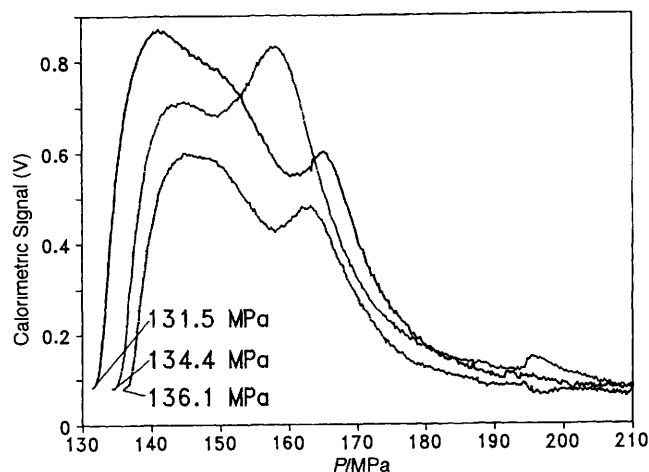


Figure 14 Isothermal recompressions at 370 K of (4-pentylphenyl) 4-decyloxythiobenzoate at a rate of 5 kPa s^{-1} started at various pressures of the coexistence of phases¹³

and transitions from chaos to order. Data on temperature induced transitions can be easily realized in such investigations under various pressures and the analysis of results performed with methods already described in the literature.²⁹ But data on pressure induced transitions can also be realized, and such investigations can sometimes be much more interesting than studies of temperature induced transitions. However, in such studies problems related to the initial rate of the transformation can create difficulties in determination of the degree of completion of the process under investigation.

5 Conclusions

Scanning transitiometry is a further development of calorimetric techniques made possible by the use of modern computers. This combination of calorimetry with volumetric techniques allows new insights into thermodynamic relations. The combination of calorimetric and volumetric information makes it possible to obtain a complete thermodynamic description of a transformation in one study. It would be even more interesting to be able to add simultaneous structural information, which would help in recognizing successive transitions. The present article presented only a basic description of the transitiometric technique. The author hopes it will stimulate further developments of both the technique and its applications.

An important field of future applications for scanning transitiometry is materials science. As was shown on selected examples of studies of liquid crystals, materials can be investigated for both thermal and mechanical stability under variable, but well defined, thermal and hydrostatic conditions. Because the hydraulic fluid [see Fig. 5(a)] transmitting the pressure inside the experimental vessel can be replaced by any liquid or gas and the measurement performed, the technique can also be easily adapted for comparative investigations of the influence of chemical composition of the environment on the material under investigation as a function of both pressure and temperature. By comparison of results, it is possible to determine the influence of various chemicals on the material under study over large pressure and temperature ranges.

Isothermal pressure scanning should find applications to high-pressure biotechnology problems such as inactivation of microorganisms by hydrostatic pressure, high-pressure sterilization and pasteurization, investigation of the life forms near deep-sea hydrothermal vents and high pressure food processing.³⁰ One of the new important applications of scanning transitiometry in this field could be a classification of bacteria with respect to their resistance to pressure presented as pressograms.

Finally, scanning transitiometry can also be of interest in chemical and physics education, especially in teaching physical chemistry and particularly chemical thermodynamics, because phenomena can be observed on various thermodynamic planes and the influence or behaviour of particular thermodynamic variables clearly demonstrated.

6 List of Symbols

$a/\text{Pa s}^{-1}$	rate of linear pressure variation
A/m^2	active area of heat exchange
$\alpha/\text{W K}^{-1}$	static coefficient of heat exchange
α_p/K^{-1}	isobaric coefficient of thermal expansion
$b/\text{K s}^{-1}$	rate of linear temperature variation
$c/\text{m}^3 \text{s}^{-1}$	rate of linear volume variation
$C/\text{J K}^{-1}$	heat capacity
CF	control function
COR	dynamic correction
$C_{p,i}/\text{J K}^{-1} \text{mol}^{-1}$	isobaric molar heat capacity
CV	control variable
DSC	differential scanning calorimeter
F_{us}	subscript denoting fusion
$h/\text{J mol}^{-1}$	molar enthalpy
H/J	enthalpy
$k_c/\text{W K}^{-1}$	static gain of the calorimetric cell
κ_c/Pa^{-1}	isothermal coefficient of compressibility
$l/\text{J kg}^{-1}$	specific heat of fusion
$\lambda/\text{W m}^{-1} \text{K}^{-1}$	heat conductivity
(lq)	liquid phase
LSC	limiting speed characteristic
m/kg	mass
n	number of moles
p/Pa	pressure
PCSC	pressure-controlled scanning calorimeter
PID	proportional-integral-differential
PR	constant proportional to the speed of pressure variations
$q_p(T)/\text{W mol}^{-1}$	molar thermal power generated or absorbed under isobaric conditions as a function of inducing temperature variation
$q_T(p)/\text{W mol}^{-1}$	thermal power generated or absorbed under isothermal conditions as a function of inducing pressure variation
$q_T(V)/\text{W mol}^{-1}$	thermal power generated or absorbed under isothermal conditions as a function of inducing volume variation
$q_V(T)/\text{W mol}^{-1}$	thermal power generated or absorbed under isochoric conditions as a function of inducing temperature variation
$Q/\text{J mol}^{-1}$	molar heat
$\rho/\text{kg m}^{-3}$	density
$s/\text{J K}^{-1} \text{mol}^{-1}$	molar entropy
s	subscript denoting the substance under investigation
(sd)	solid phase
$S/\text{J K}^{-1}$	entropy
SF	set function
t/s	time
T/K	absolute temperature
τ/s	time constant
T_c/K	temperature of the calorimetric cell
TCSC	temperature-controlled scanning calorimeter
T_r/K	temperature of the thermostat
$\theta(t)/\text{K}$	calorimetric thermogram
$u/\text{J mol}^{-1}$	molar internal energy
U/J	internal energy
v/m^3	molar volume
V/m^3	volume
VCSC	volume-controlled scanning calorimeter
V_{in}/m^3	internal volume of the experimental vessel as "seen" by the calorimetric detector
w	subscript denoting the wall of the experimental vessel
ϵ/m	thickness of the liquid layer

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