

SCANNING TRANSITIOMETRY FOR SCIENCE AND INDUSTRY

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Abstract

Basic principle of scanning transitiometry are presented. The new technique is based on a simultaneous recording of both mechanical and thermal variables of a thermodynamic transition induced by scanning one independent variable (p , T or V) while the other independent variable is being kept constant. Examples are given for applications of the new technique in materials science such as simultaneous determination of α_p and κ_T as a function of pressure for a crystalline polyethylene at 363 K, simultaneous determination of heat and volume of transition for isothermal fusion of polyethylene at 423 K and for isobaric phase changes in TÖS5 liquid crystal (4-*n*-pentyl-phenylthiol-4'-decyloxybenzoate) at 134.6 MPa. A special attention is paid to the determination of α_p for dense liquids, theoretical interpretation of its pressure-temperature behavior and the use of the new technique in verification of equations of state for dense condensed systems.

Keywords: PE, scanning transitiometry, thermodynamics

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 [1]. In Fig. 1 is given a schematic presentation of four situations in which always one independent variable is kept constant and the other programmed as a given function of time, the resulting rate of heat exchange, if measured properly in a calorimeter, permits to determine respective thermodynamic derivatives. Temperature-controlled scanning calorimeters (TCSC), in which temperature is taken as the inducing variable and varied as a linear [2] or stepwise [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 program, so that the thermodynamic significance of the calorimetric output signal is

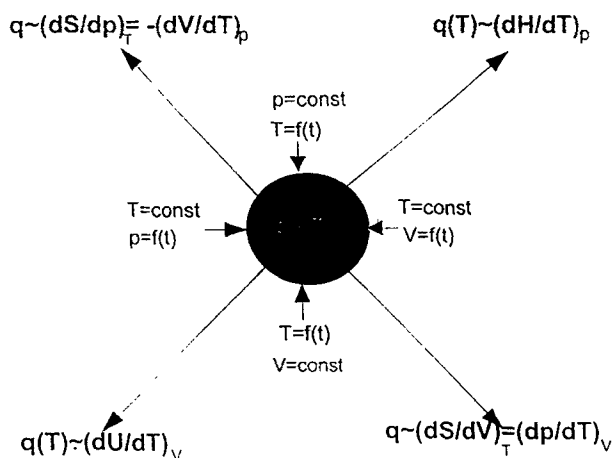


Fig. 1 A schematic presentation of relations between the inducing variable (p , V or T) and the thermodynamic significance of the thermal power q of the induced transition

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 cell [9] 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 of a system can only be a result of the perturbation of its thermodynamic state by a variation of the inducing independent variable. The possibility of controlling of 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 analyzing 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. This technique we have called **transitiometry**, from latin *transitio* -change, and greek *μετρον* – measure, because it permits direct investigation of physicochemical transitions of various types and much deeper description than could be done with separate calorimetric and/or dilatometric analysis.

Experimental

A realization of the fundamental thermodynamic principles presented above can be exemplified with some technical details and diagrams presented below and

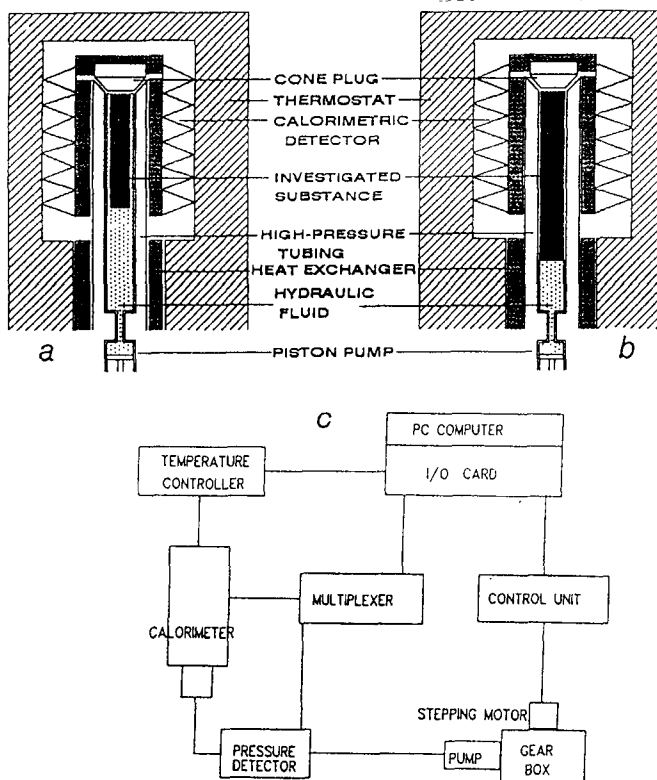


Fig. 2 Diagrams of a transitiometer: a, b, two methods of transmitting pressure into the calorimetric vessel; c, a block scheme of a transitiometer [10, 11]

which have been taken from the actual version of the instrument, that has been patented and commercialized [10, 11].

A schematic presentation of the mechano-calorimetric part of the transitiometer is given in Figs 2a and 2b, where two distinct thermodynamic situations are presented:

a) the action of pressure on the substance under investigation placed in the active part of the calorimetric vessel is exerted through a hydraulic fluid which occupies a part of the inner volume of the experimental vessel and thus the mass of the sample in the active part of the calorimetric vessel remains constant, but the thermodynamic contribution from the hydraulic fluid must be subtracted from the output signal;

b) pressure is transmitted through the substance itself; in this case the active internal volume of the calorimetric vessel is filled completely with the investigated substance and in the course of the pressure variation the mass of the sample will be equal to the ratio of the internal volume of the vessel to the molar volume of the substance, in case of linear pressure variations this leads to the direct determination of the isobaric coefficient of thermal expansion as a function of pressure [6].

A block diagram of the whole transitiometer is presented in Fig. 2c. The calorimetric vessels placed in the calorimetric detector are connected to the high-pressure pump with the help of stainless-steel capillaries. The piston of the 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. 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 volume variations are recorded by counting the number of motor steps, which drive the piston of the high-pressure pump. The recording of the motor steps leads to the simultaneous determination of the isothermal compressibility (κ_T) as a function of pressure for the substance under investigation (the compressibility of the hydraulic fluid must be taken into consideration) [9]. The total volume of the sample under investigation can be varied from 0.5 to 2.5 cm³, depending on the kind of measurement performed. Typical low scanning rates are: T : $8 \cdot 10^{-4}$ K s⁻¹, V : $2 \cdot 10^{-5}$ cm³ s⁻¹ and p : 2 kPa s⁻¹. These allow measurement near the equilibrium state for many processes. The sample can be loaded once into the experimental vessel and the phenomenon under investigation observed in various thermodynamic planes.

The software organization of the instrument realizing the four thermodynamic situations presented in the introduction together with the recording of the variations of the dependent mechanical variable is given in Fig. 3. 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. 3) 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. 3) are always heat and variations of the dependent mechanical variable (pressure or volume). This permits simultaneous determinations

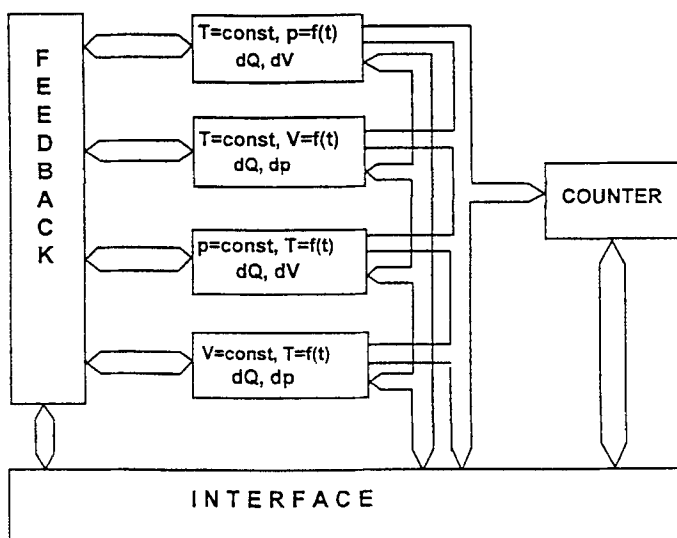


Fig. 3 Schematic diagram of the software organization of a transitiometer [10, 11]

of the following pairs of thermodynamic quantities: α_p , and κ_T , γ and κ_T , C_p , and α_p , C_V and κ_T .

A model example for scientific applications

It would be difficult to exemplify all possible applications of the new technique in a short study. For applications concerning the investigations of phase transitions the reader is advised to see previous publications [5, 12, 13]. In this study a special attention will be paid to the determination of pressure-temperature behavior of α_p and to its theoretical interpretation. At high pressures the determination of α_p by calorimetric technique for liquids is more precise than by volumetric or dilatometric techniques. A number of liquids have been already investigated by this technique [14]. It appears from those studies that for simple liquids (without strong specific interactions) the isotherms of α_p have a unique crossing point. In Fig. 4a is presented a set of isotherms of α_p for *n*-hexane, obtained from a correlation equation based on experimental data from various laboratories [15]. At low pressures, below the pressure of the crossing of isotherms, thermal expansivity increases with increasing temperature, but at higher pressures (experimentally investigated up to 700 MPa), α_p decreases with temperature increases. At the pressure of the crossing point, the coefficient of thermal expansion is independent of temperature. None of the known equations of state (EOS) can reproduce this property. The van der Waals equation of state does not reproduce any crossing of isotherms (Fig. 4b); similarly behave all the van der Waals type EOS with a modified attractive contribution to the pressure [16]. However, the Carnahan-Starling [17] modification of the repulsive

contribution to the pressure in the van der Waals EOS properly demonstrates the crossing of isotherms, although the coordinates of the crossing point are rather far from the experimental data (Fig. 4c). A recent modification of the van der Waals EOS by replacing the repulsive contribution with a soft-sphere term [18] has significantly improved its ability to reproduce the experimental data. At the moment, the best reproduction of the experimental isotherms of α_p for *n*-hexane is obtained with the soft-sphere term constructed with the use of 8-4 Lennard-Jones potential (Fig. 4d). For methane this reproduction is almost perfect [16], most probably because methane is much more spherical than *n*-hexane.

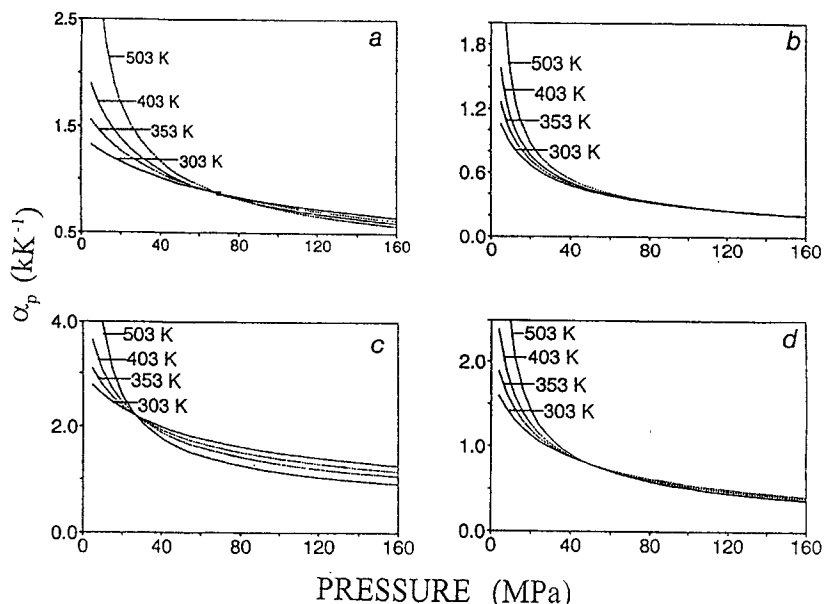


Fig. 4 Isobaric thermal expansivities (α_p) of *n*-hexane: a, experimental [15]; b, derived from the van der Waals EOS [16]; c, derived from the Carnahan-Starling-van der Waals EOS [16, 17]; d, derived from a soft-sphere EOS constructed with 8-4 Lennard-Jones pair potential [16, 18]

The above observation that the crossing point of isotherms may be reproduced better with the soft than with the rigid interacting pair potentials is to some extent similar to an attempt by the present author to explain the existence of the crossing point of α_p isotherms for simple dense liquids by the pressure-sensitive shape of the effective intermolecular potential [19].

The behavior of $\alpha_p(p, T)$ for associated liquids is much more complicated than that for the simple liquids, and depends on the mechanism of the specific interactions. For example, calorimetric measurements have demonstrated that with addition of *n*-hexanol to *n*-hexane the crossing of isotherms is pushed to higher pressures, almost as a linear function of *n*-hexanol concentration [20, 21]. This behavior could be approached only with the soft-sphere EOS [18] with an addition of a contribution to the pressure coming from the association [22]. More details on the

soft-sphere EOS for linear association in liquids will be given elsewhere. In case of *m*-cresol [23] a self-associated liquid, there is no crossing point over the temperature range from 303 K to 503 K at pressures up to 400 MPa. The isotherms do cross near 100 MPa, but the crossing points are temperature dependent. The isotherms cross at lower pressures as temperature increases. A unique crossing point may exist at some high temperature where *m*-cresol is unassociated since the low-temperature behavior probably results from the association equilibrium.

The use of scanning transitiometry in the investigations of dense liquids is an example of a complete research cycle: the macroscopic quantity α_p measured over wide ranges of both pressure and temperature in the instrument, can be also modelled through equations of state constructed on the basis of fundamental molecular properties. This possibility, together with the facility of using the instrument, should argue for exploitation of this approach also in the university education.

Examples of applications in materials science

Thermophysical properties of polymers and polymeric materials are of considerable importance both to polymer scientists and engineers. The properties of the solid polymers result very often from the coexistence of crystal and amorphous phases. This coexistence can be perturbed by a change in the external environment, such as mechanical stress, gas adsorption or gas dissolution, which can lead even to accidental irreversible transitions. For this reason the simultaneous measurements by transitiometry of both mechanical and thermal properties is of great importance, because it gives credit that the measurements are performed on a sample in the same state. In Fig. 5 is presented an example of simultaneous determination of both α_p and κ_T as a function of pressure for a linear polyethylene sample of medium density (crystallinity 0.57 mass fraction) at 363 K, near its temperature of fusion at atmospheric pressure.

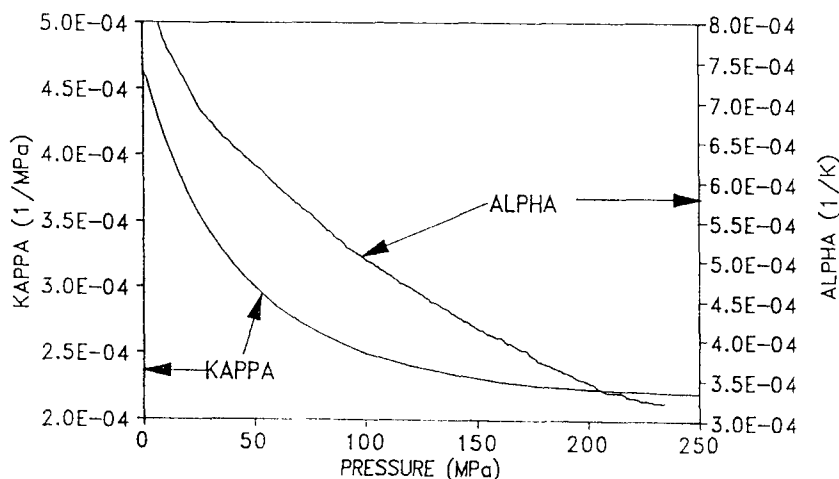


Fig. 5 Isobaric thermal expansivity (α_p) and isothermal compressibility (κ_T) of medium density polyethylene (crystallinity 0.59) determined simultaneously at 363 K

In Fig. 6 is given an example of simultaneous determination of the rate of heat exchange and of the rate of volume variations during isothermal fusion of a sample of the same polyethylene at 423 K induced by linear pressure scan with a rate

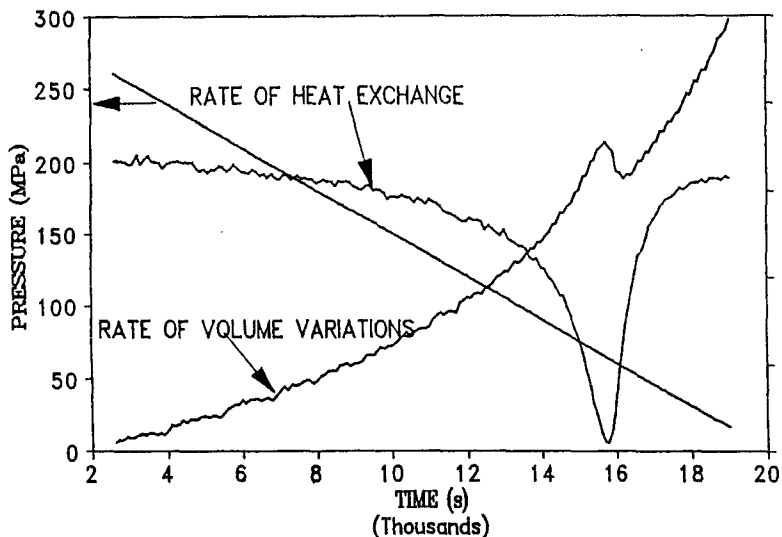


Fig. 6 Isothermal fusion of medium density polyethylene at 423 K; arbitrary units for rates of both heat exchange and volume variations

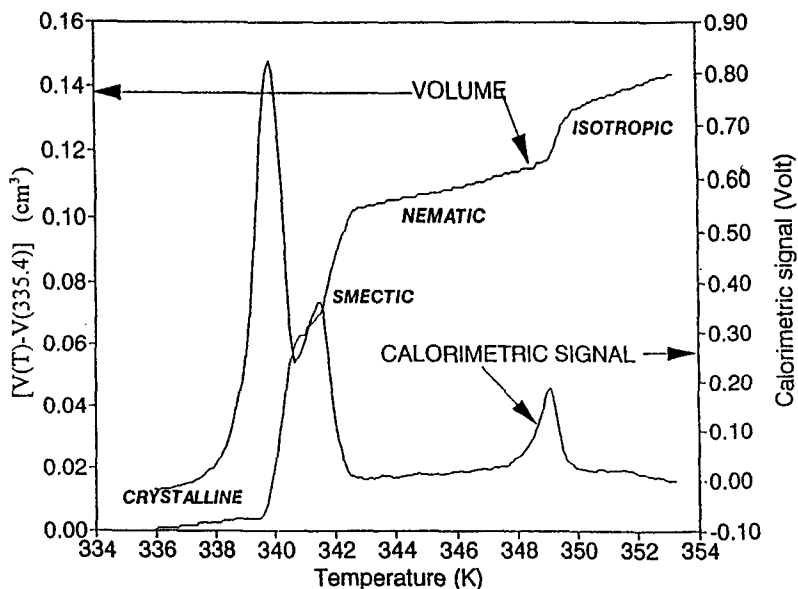


Fig. 7 Isobaric phase transitions in TOS5 liquid crystal (4-*n*-pentyl-phenylthiol-4'-decyloxybenzoate) at 134.6 MPa induced by a linear temperature decrease at 0.8 mK s^{-1}

0.015 MPa s⁻¹. An example of simultaneous recording of both the calorimetric curves and volume variations is given in Fig. 7 for multiple isobaric phase transitions in 1O55 liquid crystal (4-*n*-pentyl-phenylthiol-4'-decyloxybenzoate) at 134.6 MPa. Those transitions were induced by a linear temperature decrease with a rate 0.8 mK s⁻¹. The pressure in the system was controlled by an automatic compensation for the volume changes with the help of the piston driven by the stepping motor. From the number of motor steps used for that compensation the volume variations were determined. In this case the compressibility of the hydraulic fluid had no influence on the recorded volume variations, because the pressure in the system remained constant.

In Fig. 8 are presented thermal expansivities of crystal and amorphous phases of polyethylene as a function of pressure at 303 K and 333 K. The experimental data have been obtained for the two phases by extrapolation of data from transitiometric measurements performed for polyethylenes of various crystallinities [24]. The Pastine theoretical EOS [25, 26] has been used for derivation of thermal expansivities for the two phases at the same conditions of temperature and pressure. One can observe that for the crystal phase the agreement is reasonably good at low pressures, while at higher pressures the theoretical values diverge from the experimental data. For the amorphous phase the agreement is less satisfactory, even at low pressures. This can be attributed to the approximate character of the amorphous part in the Pastine EOS.

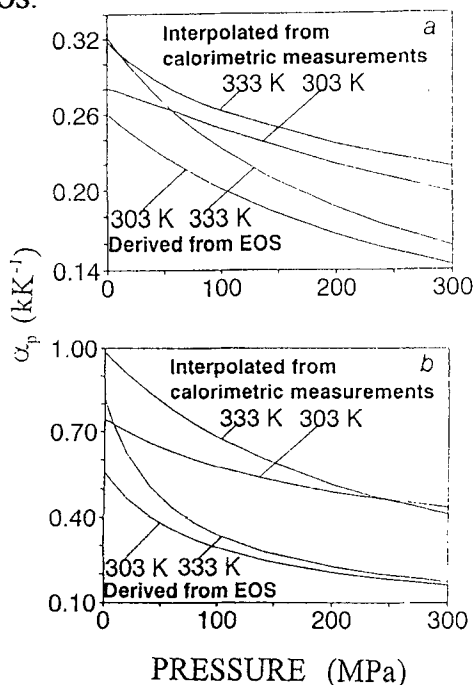


Fig. 8 Isobaric thermal expansivities (α_p) of crystal and amorphous phases of polyethylene determined by interpolation from calorimetric measurements [24] and derived from the Pastine EOS [25, 26]

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.

An important field of future applications for scanning transitiometry is materials science. As was shown on selected examples of studies of polymers and 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 transmitting the pressure inside the experimental vessel can be replaced by any liquid or gas and the measurement performed, the technique can be also easily adapted to comparative investigations of the influence of chemical composition of the atmosphere 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 life forms near deep-sea hydrothermal vents, high pressure food processing, etc. [27]. One of 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 various theoretical models, especially EOS of condensed phases [28] can be easily verified; phenomena under investigation can be observed on various thermodynamic planes and the influence or behavior of particular thermodynamic variables clearly demonstrated.

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References

- 1 S. L. Randzio, *Thermochim. Acta*, 89 (1985) 215.
- 2 M. J. O'Neill, *Anal. Chem.*, 36 (1964) 1238.
- 3 H. Staub and W. Perron, *Anal. Chem.*, 46 (1974) 128.
- 4 S. L. Randzio, *J. Phys. E*, 16 (1983) 691.
- 5 S. L. Randzio, *J. Phys. E*, 17 (1984) 1058.
- 6 S. L. Randzio, J.-P. E. Grolier and J. R. Quint, *Rev. Sci. Instr.*, 65 (1994) 960.

- 7 L. Ter Minassian and Ph. Pruzan, *J. Chem. Thermodynamics*, 9 (1977) 375.
- 8 L. Ter Minassian and F. Milliou, *J. Phys. E*, 16 (1983) 450.
- 9 S. L. Randzio, D. J. Eatough, E. A. Lewis and L. D. Hansen, *J. Chem. Thermodynamics*, 20 (1988) 937.
- 10 S. L. Randzio, J.-P. E. Grolier, J. Zaslona and J. R. Quint, Patents: 91-09227 (France), P-295285 (Poland).
- 11 BGR TECH, 04-404 Warsaw, Plutonowych 16, Poland.
- 12 S. L. Randzio, *Pure & Appl. Chem.*, 63 (1991) 1409.
- 13 S. L. Randzio, *J. Thermal Anal.*, 38 (1992) 1989.
- 14 S. L. Randzio, in *Experimental Thermodynamics, Vol. IV. Solution Calorimetry*, (P. A. G. O'Hare and K. N. Marsh, Eds.), Blackwell Scientific, London 1994, pp. 303-324.
- 15 S. L. Randzio, J.-P. E. Grolier, J. R. Quint, L. D. Hansen, E. A. Lewis and D. J. Eatough, *Int. J. Thermophysics*, 15 (1994) 415.
- 16 S. L. Randzio and U. K. Deiters, *Ber. Bunsenges. Phys. Chem.*, 99 (1995) 1179.
- 17 N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, 51 (1969) 635.
- 18 U. K. Deiters and S. L. Randzio, *Fluid Phase Equilibria*, 103 (1995) 199.
- 19 S. L. Randzio, *Phys. Lett. A*, 117 (1986) 473.
- 20 S. L. Randzio, J.-P. E. Grolier and J. R. Quint, *J. Thermal Anal.*, 38 (1992) 1960.
- 21 S. L. Randzio, J.-P. E. Grolier and J. R. Quint, *Fluid Phase Equilibria*, 110 (1995) 341.
- 22 U. K. Deiters, *Fluid Phase Equilibria*, 89 (1993) 229.
- 23 S. L. Randzio, D. J. Eatough, E. A. Lewis and L. D. Hansen, *Int. J. Thermophysics*, 16 (1995) 883.
- 24 L. Rodier-Renaud, S. L. Randzio, J.-P. E. Grolier, J. R. Quint and J. Jarrin, *J. Polym. Sci.: Part B: Polym. Phys.*, 34 (1996) 1229.
- 25 D. J. Pastine, *J. Chem. Phys.*, 49 (1968) 3012.
- 26 D. J. Pastine, *J. Appl. Phys.*, 41 (1970) 5085.
- 27 *High Pressure and Biotechnology, Colloque INSERM*, Vol. 224 (C. Balny, R. Hayashi, K. Heremans, P. Masson, Eds.).
- 28 S. L. Randzio, *Chem. Soc. Rev.*, 24 (1995) 359.