

Transitiometry

Towards a global virtual instrument control and a virtual link between experiment and modelling

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Abstract

A short recalling is given of the most important recent developments in the field of calorimetry and related techniques applied in the study of phase transitions which permit to achieve pico- and femtojoule sensitivities on the energetic scale and femtomole sensitivities on the reactant concentration scale. An emphasis is given to the global virtual instrument control which should facilitate and familiarise the techniques of measurements. A hope is expressed that the future developments should make much closer instrumental links between results of thermodynamic measurements and their molecular interpretation and that the internet facilities will enable both a closer connection between the research and the industry and a much easier and direct verification of both the new instrumentation and the results obtained. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal methods of analysis have always been widely used in investigation of phase transitions. Phase transitions are central to life on earth and understanding them is one of the prime task of condensed-matter physics, chemical physics and physical chemistry and even certain branches of biological sciences. Phase transitions are also very important in industrial practice, more and more knowledge of a phase diagram, often at extreme conditions of pressure, temperature and chemical reactivity, is a limiting factor of development of an industrial pro-

cess, as it is in the cases of precipitation of asphaltenes from high-pressure reservoir fluids, some sol-gel transitions, polymerisation under solvent near supercritical conditions, micro- and nanofoaming processes, to cite only more frequent recent examples. Very often the encountered transitions are of very complex nature and to understand them one must perform a very basic analysis. In 1933 Ehrenfest [1] classified transitions according to the lowest-order derivative of the thermodynamic potential which changes discontinuously at the transition. For example, fusion of ice is a first order transition because the thermodynamic potentials of water and ice at the equilibrium state are equal, but the first derivatives of the thermodynamic potentials at the both phases, entropies (derivatives with respect to temperature) and

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volumes (derivatives with respect to pressure) are not equal. Thus, the first order transitions are always accompanied by heat effects and volume changes; the second order derivatives, such as thermal expansivity, compressibility and heat capacity go to infinity at such transitions. The second order transitions according to the Ehrenfest classification are such at which both the thermodynamic potentials and their first order derivatives are equal at the two phases at equilibrium, but abrupt changes of the second order derivatives (heat capacity, compressibility and thermal expansivity) occur. Thus, the second order transition is not accompanied by heat effect and volume change; as a function of temperature at the temperature of the second order transition only a change of the slope of enthalpy (heat capacity abrupt change) or volume (thermal expansivity abrupt change) can be observed. This clear classification was often used in the literature until it was realised that derivatives of the thermodynamic potentials can diverge as a transition is approached without actually being discontinuous at the transition [2]. So, it is now more usual (especially among physicists) to classify transitions as first order if they have non-zero enthalpy of transition, and to lump all other transitions together as ‘continuous’ ones [2]. All those considerations are valid only for transitions between phases being at equilibrium. However, there is a number of important transitions which occur between non-equilibrium states, such as the glass transition, which normally occurs between a super-cooled liquid and a glassy state. Both states are not equilibrium phases. At the temperature of the normal glass transition there is no abrupt changes of volume or enthalpy, there is only a change of the slopes of the enthalpy and volume curves. So, only step changes of the second order derivatives are observed at the glass transition temperature. With this respect the glass transition behaves similarly to the second order transitions. However, the glassy state can relax slowly into the direction of the crystal state and then recorded derivatives have more complicated character, because they also include effects related to the relaxation enthalpy or relaxation volume changes. In the field of the soft matter one can observe a number of the glass type transitions occurring between various mesophases. There are also transitions in systems dimensionally constrained or confined, understanding of which is very important for the

advancement of science and technology. Among others this may concern substances confined in porous media, atomic or molecular films deposited or adsorbed on a substrate or macromolecular free standing films spread out across an opening. There are also numerous transitions of the binodal or spinodal type of instability, often followed by another process such as polymerisation, gelatinization, precipitation or crystallisation, etc., and which more and more become important in industrial practice. The global phase diagram from purely academic problem has become an important source of inspiration and practical knowledge in supercritical technologies, exploitation of natural gas and high-pressure deep oil reservoirs. Thermal methods of analysis always played an important role in the investigation of the phase transitions, but studies of all those transitions mentioned earlier cannot be successfully accomplished with the use of the classical thermoanalytical instruments and methods only. There is a constant need for a continuous development and improvement of instrumentation in order to match the actual tasks. With this respect a great progress has been done in recent years, but still a lot can be done with the use of modern computers, new materials and technologies. The aim of the present paper is to stress on the progress realised recently in this field and to suggest some possible ways of further development.

2. Recent developments

Developments of instrumental techniques and methods have been reviewed recently by the present author [3]. However, it is worth recalling here some of the most interesting achievements, especially with respect to the solution of problems connected to the types of transitions mentioned earlier. The investigation of many complex transitions encountered mainly in macromolecular systems, where coexistence of various types of normal and co-operative molecular motions are possible has become very stimulative after the classical DSC and frequency domain calorimetry have been combined and commercialised as a new class of instruments called temperature-modulated DSC (TMDSC) [4,5]. The main advantage of this new technique is a possibility to determine simultaneously the static heat capacity, corresponding to the

fast modes of the molecular motions, which are practically always in equilibrium, and the dynamic heat capacity, frequency/time dependent, which is due to all internal degrees of freedom with a distinct time dependence during the experiment [6]. Thus, in a single TMDSC experiment it is possible to determine both the heat capacity change and the relaxation enthalpy at the glass transition or generally speaking reversible and non-reversible components of a transition. Collections of papers concerned with this new technique and its applications have been published recently in special issues of *Thermochimica Acta* (Vol. 304/305 and 330).

In the field of dimensionally constrained or confined systems one should notice at least two impressive recent developments. One is related to the sophisticated surface chemistry and another is concerned with the creation and the role of the surface itself. In the surface chemistry one of the important problems is the interaction of a mobile molecule with an immobile surface. Adsorption calorimetry has always played an important role in investigation of this problem. The heat released per mole of a gas adsorbed is closely related to the adsorbate–substrate bond strength and can be used to give the strength of the interaction between the adsorbate and the surface in detail. However, an important step forward was made recently by construction of calorimeters with the use of pyroelectric or infrared temperature detectors and the preparation of well determined surfaces of single crystals in the form of thin films [7–11]. These calorimeters provided the first opportunity to measure accurate, coverage-dependent heats with a femtomole resolution on a well-defined surfaces, where a direct correlation with structural and spectroscopic results could be made [12]. The key advantage of the technique lies in applications to irreversible systems, where adsorption, reaction heats and bond energies have not been previously measurable for single crystal surfaces. With this technique the first experimental determination was made of the energy difference between two structural phases at a solid surface by measuring the energy associated with adsorbate-induced restructuring between a stable surface phase (Pt{100}-hex phase) and a metastable (1×1) structure [12]. Liquid-crystal free standing films form another interesting dimensionally constrained system. A construction of an instrument for simultaneous measure-

ments of heat capacity and in-plane density of thin free standing films has enabled investigation of such interesting phenomena as multicriticality, two-dimensional melting, surface-induced phase transitions, layer-by-layer transitions and dimensional crossover [13–15].

The influence of reduced dimensionality can also be evidenced by the sample size used in investigation, as for example the giant magnetoresistance in magnetic overlayers or charge-density-wave conductors. Even superconductivity in high-critical-temperature superconductors seems to be related to a kind of low dimensionality effect. This highly dynamic research field has practically remained inaccessible to traditional calorimetry. Finite size phenomena appear when one or more sides of a sample are smaller than the coherence length of a physical effect. Systems such as superconducting films, magnetic multilayers or assemblies of magnetic nanoparticles very often have too small a mass to be measured with conventional devices. In addition, in materials where low dimensionality effects are due to a certain crystalline arrangement it is often very difficult to obtain a homogeneous structure over a large sample. Thus, in every case there is a great interest in measuring samples as small as possible. The reduction of the sample size must involve increasing sensitivity. Fortunately, the development of various new types of transducers, and the increasing possibilities of electronics and computers permit very fast measurements of very small temperature differences or heat flow. Until very recently the calorimetric measurement of heat effect of a few mJ involved a very advanced technique. Today a nano differential scanning calorimeter (CSC 5100) is commercially available having a base line stability of less than 50 nJ K⁻¹ [16]. In addition, a femtojoule calorimeter was recently described [17]. The calorimeter is based on the technology of micromachined cantilevers for atomic force microscopy and the principle of bimetallic bending, the sensor element consists of a silicon or silicon nitride cantilever coated on one side with 50 nm of aluminium. An optically absorbing sample is deposited directly on the sensor structure and the different coefficients of thermal expansion of the aluminium and silicon nitride layers cause the sensor to bend as the temperature of the sensor structure changes. The use of this calorimeter has been demonstrated by photothermal absorption spectra measurements and

in determination of heat generated by the reaction of H and O over a Pt catalyst [18].

3. Scanning transitiometry

The recent developments of thermoanalytical instrumentation analysed in the preceding paragraph were concerned mainly with improvements of temperature detectors or of the preparation of investigated samples. The investigated transitions were always induced by a temperature variation (linear or modulated) or by an isothermal addition of a reactant. Thus, with such an instrumentation practically only the thermal side of a transition could be investigated. But, the possibility of controlling the three most important thermodynamic variables (p, V, T) in calorimetric measurements makes it possible to realise simultaneous measurements of changes or rates of such changes of both thermal and mechanical contributions to the thermodynamic potential change caused by the perturbation [19]. For example, simultaneous recording of both heat flow and volume changes resulting from a given pressure change under isothermal conditions 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 variation under isobaric conditions, 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 recording of both heat flow and pressure changes resulting from a given inducing volume variation under isothermal conditions leads to simultaneous determination of both $(\partial S/\partial V)_T$ and $(\partial V/\partial p)_T$ (or temperature coefficient of pressure, see Maxwell relation, and isobaric compressibility) as a function of volume at a given temperature. When referring to the Ehrenfest classification of transitions [1] one can easily understand how useful is the simultaneous recording of both mechanical and thermal derivatives in the analysis of transitions and interpretation of their nature, especially in complex systems. 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. 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. For this reason the technique was called scanning transitiometry [20]. The technique can operate over wide pressure (up to 400 MPa) and temperature (223–673 K) ranges with the stepwise or linear controlling variable changes. It was already applied in investigation of systems of various nature, such liquid-crystals, polymers, dense liquids [21,22]. The technique of scanning transitiometry is particularly useful in determination of pressure effects on various phase transitions at polymeric systems [23] and in measuring the thermomechanical coefficients in the vicinity of the critical point [24]. Recently the technique was adapted to study transitions in polymeric systems under pressure of compressed supercritical fluids (SCF) [25]. Employing SCF during polymer processing allows the unusual properties of SCF to be exploited for making polymer products that cannot be obtained by other means. The supercritical transitiometer permits study of the interactions of SCF with polymers during processing under well-defined conditions of temperature and pressure. The supercritical transitiometer allows pressure to be exerted by either a SCF or a neutral medium (such as mercury) and enables simultaneous determination of basic parameters of a transition. This permits determination of the SCF effect on modification of the polymer structure at a given pressure and temperature and defines conditions to allow reproducible preparation of new polymer structures. Study of a semicrystalline polyethylene by this method has defined conditions for preparation of new microfoamed phases with good mechanical properties. The low densities and microporous structures of the new materials may make them useful for future applications in medicine, pharmacy,

or the food industry, for example [25]. The supercritical polymer transitionometry can be very easily adapted to investigation of other types of transitions, such as precipitation or crystallisation from a supercritical phase. Scanning transitionometry should also be very helpful in teaching thermodynamics and materials science. Any transition (fusion of benzene for example) can be induced by a variation of any of the external parameter (p, V, T) and observed by recording heat flow thermogram and variations of the dependent mechanical variable. The analysis of measurements and of obtained results can be very instructive for students [20,21].

4. Towards a global virtual instrument control

One can say that the scanning transitionometry is a further development of calorimetric scanning techniques made possible by the use of modern computers. The existing transitionometric instruments operate with computer programmes written with text-based languages, such as BASIC and PASCAL and the communication with the instrument itself is done through parallel or serial ports. Recently we have elaborated a new transitionometric instrument which is controlled with the use of a software created with LabView graphical programming language and the communication with the particular elements of the instrument is done through a cable connector block and a PCI/MIO board with E Series architecture. A detailed description of the new transitionometer will be given elsewhere. In the present contribution only some general remarks will be presented in order to demonstrate the main features of the new instrument. The calorimetric detector was made from 500 thermocouples assisted with a nanovolt amplifier. The calorimetric detector is placed in a metallic block directly controlled by a fully digitised temperature control loop. The readings of the control temperature detector is done with a resolution of 22 bits and transferred to the computer. The mathematical part of the PID temperature control is performed in the computer itself. Then the controlling signal is sent to the heater through a digital power supply also with a resolution of 22 bits. The calorimetric block is surrounded by a heating shield which is controlled in such a way that the temperature difference between the calorimetric block and the shield is

kept constant [26]. The pressure and volume are controlled by a piston pump driven by a stepping motor and the steps are counted by the computer. The digital pressure control loop is organised according to the previous principles [19]. The programme is organised at three main levels: front panel, block diagrams and a hierarchical structure.

The front panel, or the interactive user interface, simulates on the computer screen the panel of a real instrument. It contains knobs and push buttons of the temperature, pressure and volume controls. The four basic parameters: temperature, pressure, volume and calorimetric signal and the two heating powers (calorimetric block and heat exchange loop) are all displayed both graphically and digitally on the screen front panel.

There are several dozen of block diagrams constructed in graphical programming language which show in pictorial way all the connections and contain the source code.

The hierarchy scheme represents graphically the whole organisation of the program and is very useful, especially if something is wrong, because the operator can directly operate any of the subprograms responsible for the functioning of particular subsystems of the transitionometer.

The possibility of observing simultaneously the most important operable variables of the instrument during an experiment creates a completely new situation, because it permits to link the modelling phase of the instrument with its real functioning. The virtual instrument control has transferred transitionometry from classical push-button devices, even done with an advanced computer keyboard, to a directly interactive technique. Direct visual and simultaneous observation of the most important variables (p, T, v, Q) of a process under investigation in the course of its development is very stimulating and instructive not only for students, but also for experienced people. But the advantages of the new instrument go much further. The full digital control not only permitted to realise almost ideally the conceived model of the instrument, but also enabled to obtain much higher sensitivity and accuracy of measurements. For example, the temperature control both in constant and in scanning modes is done with a precision of one tenth or a few tenths of mK over the temperature interval of 400 K, and the scanning rates can be as low as 0.5 mK s^{-1} which permits to make

precise measurements at various thermodynamic conditions, but always as close as possible to an equilibrium state of the system under investigation and this can be done under pressures up to 400 MPa. With such possibilities the transiometer with a virtual instrument control can be applied to study most of the complex transitions mentioned in the introduction, what is a challenging task for the beginning of the 21st century.

The internet facilities can be taken as a typical element connecting the two centuries. Due to the full digital control on the Windows level, the new transiometer shortly presented above can be installed in a laboratory and be fully controlled and observed from another place, separated by any distance, with the use of the Microsoft Netmeeting programme, for example. This will create completely new possibilities in a near future, especially in relations between research laboratories, in contacting research and industrial partners, research and teaching, but also servicing, promoting and verifying the new instrumentation and the results obtained.

5. Towards a virtual link between experiment and modelling

A review of recent literature, clearly demonstrates, at least by the number of publications referred by the Chemical Abstract Service, that calorimetry and related techniques are still alive, are adapting to the requirements of the developing world and are contributing to the advancement of science and technology and this is occurring despite impressive developments observed in spectroscopic and microscopic techniques. However, the spectroscopic and microscopic techniques are often considered as being something better, because they are much closer to the molecular properties which can be today modelled or calculated with a great precision. However, without contesting those opinions it is worthwhile noting that like a microscope and a telescope have their roles to play, the spectroscopic and calorimetric techniques must coexist. It is true that molecular interpretation of data derived from thermal measurements was much less developed in recent years than such interpretations of spectroscopic data, some progress however has been made and with the new possibilities, espe-

cially coming from the virtual instrument control, the molecular modelling can be in the near future directly linked with the experiment.

Heat capacity change at the glass transition and the relaxation enthalpy can be taken as an example. From the thermodynamic point of view the isobaric heat capacity is directly proportional to the mean square amplitude of the equilibrium fluctuations in the enthalpy of a system and can be derived directly from the partition function. Because the thermodynamic heat capacity is defined as a long time average, it contains no information about the dynamic characteristics of the enthalpy fluctuations. That information is contained in the normalized autocorrelation function [27], the measurement of which is a central concern for the spectral resolution of enthalpy fluctuations. Linear response theory and the fluctuation–dissipation theorem indicate that the enthalpy autocorrelation function is accessible, in the frequency domain, from stationary temperature perturbation experiments, the relevant observable being a frequency dependent heat capacity [27]. From the frequency dependence of the heat capacity the relaxation times of the enthalpy fluctuations can be determined. A molecule existing in thermodynamic equilibrium between different conformations undergoes dynamic structural fluctuations between the various states that are accessible to it under the externally imposed conditions. According to the fluctuation–dissipation theorem, the dynamics of those fluctuations are characterised by the same parameters that characterise the return to equilibrium after a small external perturbation. The natural frequencies of the normal modes of the spontaneous fluctuations are related to the frequencies at which the system can optimally absorb thermal energy. The relaxation times for the normal modes are given as the inverses of the natural frequencies, and they characterise the frequency dependence of the apparent excess heat capacity [28]. So, a frequency-domain or multifrequency calorimeter is a thermal low frequency spectrometer.

Another example are the equations of state. The equation of state is a powerful and universal tool for describing the properties of matter. Most interesting are theoretical and semi-empirical equations of state, in which the parameters have clear physical significance, for example, they can be related to the form of the intermolecular potential [29,30]. From such equations of state some thermodynamic derivatives can be

calculated. The same derivatives can be directly measured in a p, v, T -controlled scanning calorimeter or a transitiometer. Such an approach was already used for the experimental verification of equations of state for dense liquids [30,31], but in the near future the transitiometric measurements can be modelled with proper equations of state on line in a measuring system with the global virtual control.

Of course in the literature one can find much more examples where the calorimetric or thermodynamic data are modelled with molecular models and it is a hope of the present author that the developments of new calorimetric and thermoanalytical instrumentation will go in a direction that will shorten the distance between the measurements and their basic molecular interpretation.

6. Conclusion

The last decade of the ending century has been very fruitful in impressive developments of thermoanalytical and calorimetric instrumentation. Completely new devices have been constructed with pico- or femtojoule sensitivity on the energetic scale and femtomole sensitivity on the reactant concentration scale. The developments of computers have permitted elaboration of new classes of instruments such as temperature modulated differential scanning calorimetry and scanning transitiometry. New possibilities in computer control such as, the virtual instrument approach with graphical programming, create new perspectives. First of all, an easy access to the particular blocks of the controlling programme and their clear physical significance helps to familiarise the technique of measurements, usually considered as difficult and complicated. On the other hand the new computer possibilities should stimulate the incorporation of the molecular interpretation of the experimental results into programmes of a global virtual instrument control. The recent impressive developments and clear prospects for the near future warrant that the calorimetry and related techniques will continue to contribute fruitfully to the advancement of science and technology in the new century.

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