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Fluid-phase calorimetry and more: A longtime relationship with chemical thermodynamics

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Abstract

Heat-of-mixing calorimetry has been the starting point of a long dedication of the author to chemical thermodynamics as applied to different fields of theoretical as well as practical interests. From the heat of mixing measured at room temperature and normal pressure to heat capacities and mechanical coefficients measured over extended ranges of temperatures and pressures, from fluids to polymers, several milestones mark a passionate quest for a better understanding of the thermodynamics of molecular interactions in fluid mixtures and of phase changes in polymers. © 1997 Elsevier Science B.V.

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1. Introduction

More than thirty years ago, the kinetics of esterification helped me to realize that molecular interactions played an extremely important role in liquid mixtures. Evidently, alcohols and esters being involved, their mutual interaction had to be known. Besides spectroscopic evidences of hydrogen bonding, there was a need to quantitatively evaluate the energy involved on mixing. Heat-of-mixing calorimetry provided a direct access to, and addressed the complex problem of molecular interactions and chemical thermodynamics. At this stage, I must confess that I never dealt with kinetics but, for sure, I have been engaged for over three decades in heats-of-mixing measurements and interpretation. During this period, calorimetry emerged as a rather versatile technique and, thanks to close cooperation with eminent calorimetrists, its development towards new areas of application simply convinced me that, by far, this technique is both the foundation and the main tool of chemical thermodynamics. In this paper, I want to stress how, from simple heat-of-mixing calorimetry to elaborate high-temperature high-pressure *pVT*-calorimetry, the technique has helped further the limits of understanding not only of nonelectrolyte mixtures in the liquid state but of gaseous systems as well as polymeric materials. In this passionate incursion, novel designs and experimental measurements have generated new pertinent data which were instrumental for further developments of theoretical models.

After reviewing the main steps of heat-of-mixing calorimetry and then of heat-capacity calorimetry for liquid mixtures, the subsequent developments of calorimetric techniques to measure thermochemical quantities of fluids, liquids and gases, will be con-

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sidered to eventually lead to calorimetry as a *pVT*-technique in investigating fluids as well as polymers.

2. Heat-of-mixing calorimetry

As for everyone else, the (mine) first step was to construct a colorimeter. Combining inexpensive components and accurate measurements was challenging. The final version [1] was a batch-type calorimeter using Meccano® parts, where component 1 was placed in a rotating compartment immersed in component 2, contained in a Teflon light-weight calorimetric vessel which, in turn, is placed in an isothermal Dewar flask. Upon mixing, the bottom (made of an aluminium foil) the rotating compartment was cut with a spring activated cutter. This set up was able to measure endothermal heat effects at the price of lengthy electrical calibration runs, tedious calculations for vapour-phase correction and numerous weighings. Thousands of weighings yielded hundreds of data points, particularly for binary alcohol + ester mixtures [2,3]; these and other measurements on mixtures containing chlorohydrocarbons are still the only ones existing in the literature, to be used for model calculations [4,5].

From batch calorimeter with vapour space to batch calorimeter without vapour space, the next step was the use of a Calvet-type commercial calorimeter, the CRMT calorimeter from Setaram. Mercury served to eliminate vapour spaces and an electrical heater inserted inside the mixing cell could be use for in situ calibrations [6]. With such a set up measurements on volatile substances were possible, including exothermal heats of mixing. Systematic studies, typically on alkenes + alkanes binary mixtures [6] and on esters + hydrocarbons binary mixtures [7] delivered accurate data for model calculations using group contribution models.

The end of the sixties witnessed an impressive evolution in heat-of-mixing calorimetry. Cumbersome batch-type calorimeters were progressively abandoned and flow techniques took over; however, van Ness-type dilution calorimeters were at their apogee in terms of precision and accuracy. Interestingly, in 1969, the then new Journal of Chemical Thermodynamics was instrumental in publishing in its first year issues dilution calorimeters at their best [8,9], novel approaches using flow techniques [10,11] and the newly designed Picker-type differential flow microcalorimeter [12]. I had the privilege to be in the midst of this calorimetry revolution. During 1972–73, at the NRCC in Ottawa, I had the opportunity to work with an ultimate version of the van Ness-type dilution calorimeter due to Murakami and Benson [9] and take part in the development of the use of the LKB flow calorimeter [13]. However, it was most exciting to measure for the first time enthalpies of mixing by a continuous scanning of concentration to obtain in one single run the entire mixing curve using the Picker dynamic flow calorimeter [14]. This was obtained after nights and days of nonstop laboratory sessions together with Patrik Picker, including a 52-hour session during which the author fell asleep and dropped from the stool one night. Although we showed it was possible to perform measurements under scanning, this procedure was never used but, since that time, and for more than two decades we measured heats of mixing by ‘Pickering’ under steady conditions at given concentrations [15]. Hundreds of binary mixtures, when investigated, produced a large database for different classes of organic mixtures. These measurements helped, among other things, to show that plate-like molecules of the 1,2,4-trichlorobenzene type can induce conformational changes in *n*-alkanes which manifest themselves by a decrease of the excess enthalpies when the *n*-alkane chain length increases [16], as shown in Fig. 1. As a matter of fact, this induced conformational change phenomenon, known as the *Wilhelm effect*, is one of the milestones of a long standing collaboration with Emmerich Wilhelm; numerous other solvents and systems were investigated, always looking to both the H^E and $C_p{}^E$ behaviour as reported in the following.

Naturally, flow techniques were well-suited to be adapted to perform measurements at elevated temperatures and pressures: this was superbly demonstrated by the calorimetry group at Brigham Young University, which designed several instruments making use of a heat-sink-type thermal detector–see, for example, the latest developments in [17,18] and references therein (see the contribution by J.B. Ott in this volume). We decided to use, instead, a Calvet-type differential thermal detector. For this, a C80 calorimetric unit from Setaram was equipped with a special assembly which featured a set of flow-through mixing

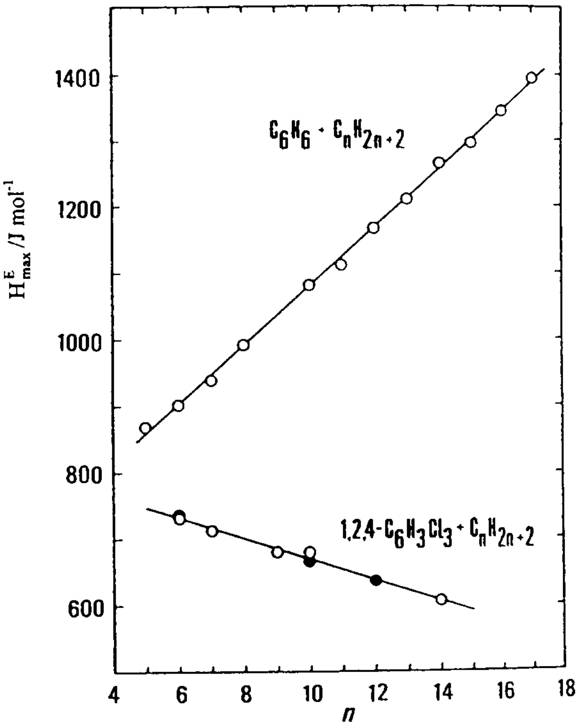

Fig. 1. Binary mixtures {benzene + n-alkane} and {1,2,4-trichlorobenzene + *n*-alkane} at 298.15 K. Dependence of the maximum molar excess enthalpies H^E_{max} on chain length *n*, of the *n*-alkane; from [16].

cells and an active heat exchanger to bring the fluids to be mixed to the working temperatures [19,20]. The design of the cells consisted of a coil made with a thin capillary tubing (1 mm i.d.) and confined in stainless steel cylinders which actually fitted into the detector thermopile. The heat exchanger worked as a counter-current heat exchanger between the two incoming fluids and the fluid mixture coming out from the mixing cell. The flow controlling system consisted of a double syringe metering pump (Brownlee Micro-feed pump). Pressure control in the entire fluid was assured by means of a back-pressure regulator. This allowed to operate the setup with either gases or liquids. A more elaborate version has been recently developed using also the differential heat-flux calorimeter, Setaram C80. In this set up [21] the mixing cell also consists of a stainless steel tube (1.6 mm o.d., 0.3 mm wall thickness) tightly coiled in ~45 loops in a metallic confinement cylinder which fits into the thermopile detector of the calorimetric block. An identical mixing cell, serving as a reference, is placed in the second thermopile without any connection to the fluid circuit. The main difference with the previous setup concerns the calorimetric head and the counter-current heat exchanger with a preheater. The heat exchanger consists of three tubes (1.6 mm o.d.) twisted together side-by-side over the length of 1.0 m in such a way that both the incoming fluids are circulated in one direction whereas the fluid mixture coming out from the cell is circulated in the opposite direction. A heating tape serving as an active preheater is wrapped around the three tubes. After passing through the heat exchanger, the incoming fluids reach the calorimetric head, a 'T'-joint piece, which makes it possible to introduce the fluids in two concentric tubes descending from the head vertically into the coiled mixing cell; the outer tube eventually connecting with the coiled tubing itself. This head also plays the role of ultimate fine thermostat for the fluids entering the mixing cell; for this purpose, the 'T'-joint piece holds two heaters and a platinum resistance temperature detector. The whole setup was checked with different test systems at temperatures up to 530 K and at pressures up to 20 MPa; it was mostly used to measure heats of absorption of carbon dioxide in aqueous solutions of alkanolamines [22] to correlate enthalpies of absorption and solubilities obtained therefrom [23] .

In the move for obtaining data faster, more accurately and, simultaneously, data on important thermodynamic quantities, we have developed a new type of flow instrument, combining a heat-of-mixing calorimeter and a vibrating-tube densimeter [24]. The calorimeter and the densimeter are housed in the cavity of a thermo-regulated massive block which also serves for final preheating of the fluids before mixing; the block itself is surrounded by a system of heated cans and lids. The densimeter is connected in series to the exit of the heat-of-mixing calorimeter in such a way that under flow conditions, and for a given concentration, heat of mixing is first measured in the calorimeter and thereafter, the corresponding density measurement is taken in the densimeter. The vibrating-tube densimeter has been described previously [25]. The calorimeter is made of one aluminium piece and consists of two cylindric hollow sections. The lower one (39 mm o.d., 41 mm height, 4 mm thick wall) is immersed in a cavity of the block and supports the tubing, regulation and compensation heaters, and a regulation thermometer. The upper section (28 mm o.d., 41 mm height, 5 mm thick wall) serves for transporting the heat from the calorimeter towards the heat sink. With such design the heat effect measurements are based on the heat conduction and heat compensation principle across the heat conductor between the calorimeter proper and the heat sink. The entire setup has been satisfactorily tested by mixing experiments with the methanol + water and ethanol + water systems; measurements can be performed at superambient conditions up to 573 K and pressures up to 30 MPa.

3. Heat-capacity calorimetry

Undoubtedly, Picker's contribution to this field is invaluable. The 1969 case history paper [12], followed by a second in 1971 [26], on measuring heat capacities of liquids under flow conditions with a differential thermal balance method saw the initiation of modern heat capacity calorimetry for liquids. Again, in 1973, I had the privilege to learn and use this technique with Patrick Picker. As a first step, we showed it was possible to directly and simultaneously measure densities and heat capacities on the same liquid sample flowing through a heat-capacity calorimeter and a vibrating-tube densimeter (of Picker's design) hooked in series [27]. Concomitantly, we also established the step-wise method for measuring a series of mixtures in the order of increasing concentration of one of the components; starting from zero mole fraction, each mixture was used as a reference liquid for the next in the series. This procedure restricted the determinations of volumetric specific heats to small differences which could be measured to full sensitivity. Simultaneous heat-capacity/density measurements were never taken routinely but combined measurements (each type of measurement taken independently) have been the rule since then. For our part, in two decades (1973–1993) we produced the largest database on binary organic mixtures of different types: this appeared in more than 40 papers with a rough estimate of 150 systems. Among the systems investigated, the most striking result was obtained in collaboration with Inglese and Wilhelm; it concerned the *unusual composition dependence* of excess molar heat capacity of {1,4-dioxane + an n-alkane} binary mixture [28] as shown in Fig. 2. Typically, the $C_p{}^E$-curve plotted against the mole fraction of the cyclic ether showed a double minimum separated by a marked maximum, yielding a *W-shaped curve*. Such a behaviour was recognized as the consequence of the existence of preferential orientations and aggregations of some *flexible molecules* in admixture with similarly flexible alkanes, depending on the concentration range. For many years since this behaviour was reported, W-shaped $C_p{}^E$-curves, including theoretical modelling, were obtained in several laboratories worldwide (see, for example, [29] and references therein). For our part, we found such behaviour typically for mixtures containing ketones [30], α-ω,dichloroalkanes [31–33], and alkanoates [34,35]. As a matter of fact, the number of systems known to show such W-shaped $C_p{}^E$-curves has increased steadily, and this behaviour is now recognized as being of relatively wide occurrence in mixtures of a strongly polar substance and an n-alkane, although it is not restricted to this kind of systems alone. In this context, the correlation of W-shaped $C_p{}^E$-curves with concentration fluctuations [36–38] is particularly interesting.

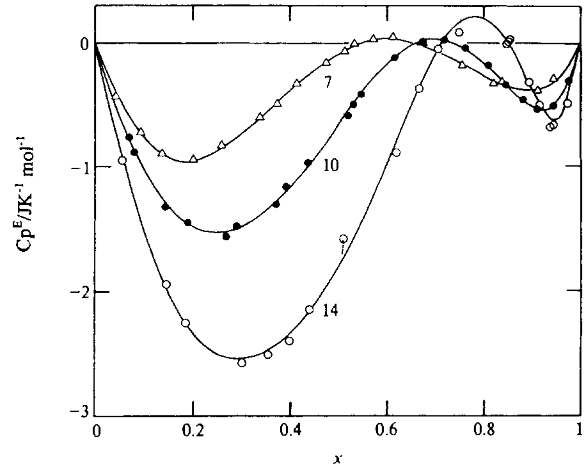

Fig. 2. Excess molar heat capacities $C_p{}^E$ at constant pressure of binary mixtures {1,4-dioxane + n-alkane} at 298.15 K as a function of the mole fraction x of n-alkane; labels corresponds to the number of carbon atoms of the n-alkane; from [28].

Like for heats of mixing, there was a need for heat-capacity measurements performed at elevated temperatures and pressures. Extension of the Picker design to enable measurements to be made over large temperature and pressure ranges was made in several laboratories. The one due to Wood and Smith-Magowan [39,40] has been basic for most subsequent calorimeters. Our contribution in the field of heat-capacity measurements over extended temperature and pressure ranges make use of Calvet-type differential heat flux detectors equipped with special cells in which measurements are taken in the static mode (no fluid-flow) [41]. Between 270 and 370 K, at atmospheric pressure, we used a programmable differential scanning calorimeter (micro-DSC from Setaram). This apparatus has essentially two thermopiles inserted in a thermostatted metallic block; two small sized (1 cm^3), batch-type cells are tightly fitted in the thermopiles. A liquid thermostat ensures the temperature control of the metallic block to within ±1 mK. A detailed description and operating mode have been reported together [42–44]. Between 300 and 570 K, we used a Setaram C80 calorimeter with which operation is similar to the one with the micro-DSC; the temperature of the thermostatted block containing the thermopiles and cells is brought to the required value by means of an electric heater (instead of a liquid-filled thermostat). An initial version [45] of the set up was designed to study concentrated aqueous salt solutions [46]. A more recent version for measuring heat capacities of gases has been described in details elsewhere [47]. The entire experimental assembly, shown in Fig. 3, features two cylindrical cells (inner volume $\approx 11\ cm^3$), made of stainless steel, which have been specially designed to sustain temperatures up to 573 K and pressures up to 30 MPa. The temperature is read to 0.06 K by means of a 100 Ω platinum resistance, located between the two cells. The operation of the instrument is made in the static mode and, in order to eliminate heat leaks by conduction and connection through the connecting tubes of the cells, an additional thermostat was mounted on the top (the 'head') of the calorimeter (see Fig. 3); additional thermal guards

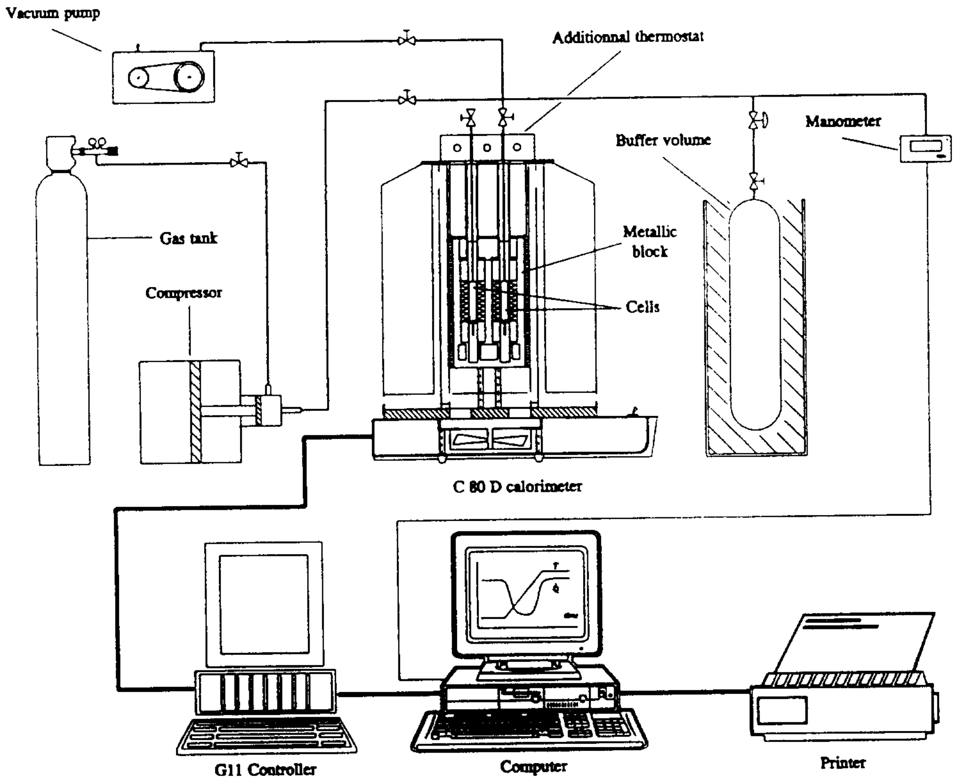

Fig. 3. Schematic diagram of the set up for measuring heat capacities of gases with a C80 Setaram calorimeter, from [48].

around the connecting tubes further improved the temperature control of the cells. In actual experiment, constant pressure during heating or cooling is monitored through the use of a buffer volume connected to the sample cell. This buffer consists of two 0.5-1 cylinders connected together and placed inside a cylindrical thermostatted block. With such an arrangement, pressure inside the cell can be read with a accuracy of 0.5% of the full scale of a 50 MPa pressure gauge. The whole set up operation is monitored by a computer through an RS-232 interface; a typical constant pressure experiment, covering the 323–423 K range and consisting in measuring C_p at ten different selected fixed temperatures, can be run fully automated in 24 h. This calorimeter and associated experimental procedure have been advantageously used to measure heat capacities of various gases (pure gases and mixtures); of special interest was the study in the vicinity of the critical points [48].

4. Thermodynamic derivatives by pVT-calorimetry

For a thermodynamicist, *pVT*-calorimetry is surely the most accomplished experimental concept [49]. It allows a direct determination of the most important thermodynamic derivatives; it shows how, in practice, Maxwell relations can be used to fully satisfy the thermodynamic consistency of those derivatives. In this respect, Stanislaw Randzio's contribution has been essential [50], especially in showing how the thermodynamic functions of a system can be accurately determined by measuring their derivatives against an independent thermodynamic variable.

Also of particular interest is the use of pressure as an independent variable [51–54]. This is typically illustrated by the newly established pressure-controlled scanning calorimeters (PCSC) [55,56] and it has been my pleasure to participate with Randzio in developing these techniques which opens a new era in thermodynamics. Basically, the isobaric expansivity $\alpha(p, T) = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$ can be considered as the key quantity from where the molar volume v can be derived and therefrom all subsequent molar thermodynamic derivatives with respect to pressure, T_0 being a reference temperature:

$$v(p, T) = v(p, T_0)\exp\left\{\int_{T_0}^{T} \alpha(p, T)dT\right\} \tag{1}$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v(p, T_0)\exp\left\{\int_{T_0}^{T} \alpha(p, T)dT\right\} \tag{2}$$

$$\left(\frac{\partial h}{\partial p}\right)_T = v(p, T_0)[1 - T\alpha(p, T)] \times \exp\left\{\int_{T_0}^{T} \alpha(p, T)dT\right\} \tag{3}$$

$$\left(\frac{\partial s}{\partial p}\right)_T = v(p, T_0)\alpha(p, T)\exp\left\{\int_{T_0}^{T} \alpha(p, T)dT\right\} \tag{4}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -Tv(p, T_0)\left[\alpha_T^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p \times \exp\left\{\int_{T_0}^{T} \alpha(p, T)dT\right\}\right] \tag{5}$$

Knowing the molar volume as a function of p at the reference temperature T_0, the determination of the foregoing pressure derivatives only requires the measurement of the isobaric expansivity α as a function of p and T. Thus, it is easy to compute the total variations of the above-mentioned thermodynamic functions over extended p, T-surfaces.

Pressure-controlled scanning calorimetry is so versatile and, in fact, so easy to operate that it makes thermodynamics easier to understand, and to use in many applied fields; it is also a perfect tool to teach thermodynamics (and attract new followers or passionate thermodynamicists). Complete and comprehensive investigations on pure components like *n*-hexane [57] or 1-hexanol [58], on binary *n*-hexane + 1-hexanol mixtures [59,60] or in the vicinity of the critical point [61], typically demonstrate the power of the technique to provide a full and extended thermodynamic description of systems under study.

5. Scanning transitiometry

Another promising development of thermodynamic variable-controlled scanning calorimetry is its extension to study phase transitions [62]. The advantage of controlling the three main thermodynamic variables p,

V and T during calorimetric measurements and therefrom of determining simultaneously thermal and mechanical effects, allows to investigate systems having limited stability or showing transitions. That is to say, not only is the complete thermodynamic description of the system possible but transitions can be analysed in detail or even monitored along changes of the state variables.

From this point of view transitiometry has performed very well to investigate polymers. The best example is the complete study of the behaviour of the thermal expansivity α_p of various polyethylenes as a function of pressure, temperature and density (or crystallinity) [63]. One of the striking results is the linear decrease of α_p with the degree of crystallinity over the 0–300 MPa pressure range. This linear dependence allowed to estimate α_p for both the crystal and the pure amorphous phases as functions of pressure up to 300 MPa. At 302.6 K and 0.1 MPa, the estimated α_p of the crystal phase is equal, within the experimental error, to the literature value of α_p for the orthorhombic polyethylene unit cell derived from crystallographic data. Another interesting example of the use of the transitiometric technique is the study of the influence of temperature and pressure on the fusion of polyethylenes, particularly in the prefusion region [64]. Fig. 4 shows experimental isobaric curves of a medium density polyethylene as a function of temperature; typically, at low pressure, α_p sharply increases in the premelting zone. Presently, the technique is used to investigate the influence on the thermomechanical properties, as well as on their fusion and crystallisation, of polymers in which supercritical gases are dissolved.

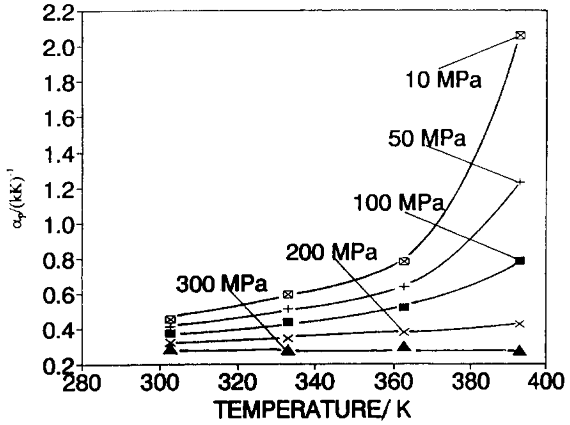

Fig. 4. Thermal expansivity α_p of a medium density polyethylene plotted against temperature at five different pressures between 10 and 300 MPa.

6. The present and the future

For many years, my efforts have been directed towards the development of new experimental techniques and their use in obtaining reliable data on many different systems. However, the aim was not only for calorimetry per se. Calorimetry is a sophisticated tool providing the best information to carry out research projects in various fields of interest. I am not here dealing with theoretical interpretation of the results, neither with specific applications. Evidently, new designs and improved capabilities of calorimeters have constantly enlarged the horizon of possible and practical applications for modern thermodynamics. Of particular importance is the introduction of pressure as a scanning parameter. It turns out that working with high pressures is relatively easy and that calorimetry has naturally gained more importance in the thermodynamic description of matter and of its transformation. Certainly, materials science is a major field for future applications; the study of polymers submitted to the triple stress, temperature, pressure, and dissolved gases should bring new insights into the behaviour of such important materials present in our everyday life.

Isothermal pressure scanning should find application in fields as different as high pressure fluid technology, high temperature, high-pressure food processing or high-pressure biotechnology.

As a calorimetrist and thermodynamicist, I am proud of the existing stage of calorimetric techniques, I am also convinced that new developments, for example 'nano' replacing 'micro' are opening new perspects. In other words, an *"old technique" stays in the forefront of science and helps thermodynamics push new frontiers.*

References

[1] J-P.E. Grolier and A. Viallard, J. Chim. Phys., 67 (1970) 1582.

[2] J-P.E. Grolier and A. Viallard, J. Chim. Phys., 68 (1971) 1442.

[3] J-P.E. Grolier and A. Viallard, J. Chim. Phys., 69 (1972) 2030.

[4] J-P.E. Grolier, K. Sosnkowska-Kehiaian and H.V. Kehiaian, J. Chim. Phys., 70 (1973) 367.

[5] J-P.E. Grolier and H.V. Kehiaian, J. Chim. Phys., 70 (1973) 807.

[6] M.H. Karbalai Ghassemi, J-P.E. Grolier and H.V. Kehiaian, J. Chim. Phys., 73 (1976) 925.

[7] J-P.E. Grolier, D. Ballet and A. Viallard, J. Chem. Thermodynamics, 6 (1974) 895.

[8] R.H. Stokes, K.N. Marsh and R.P. Tomlins, J. Chem. Thermodynamics, 1 (1969) 211.

[9] S. Murakami and G.C. Benson, J. Chem. Thermodynamics, 1 (1969) 559.

[10] J. Sturtevant and P.A. Lyons, J. Chem. Thermodynamics, 1 (1969) 201.

[11] M.L. McGlashan and M.F. Stoeckli, J. Chem. Thermodynamics, 1 (1969) 589.

[12] P. Picker, C. Jolicoeur and J.E. Desnoyers, J. Chem. Thermodynamics, 1 (1969) 469.

[13] R. Tanaka, P.J. d'Arcy and G.C. Benson, Thermochim. Acta, 11 (1975) 163.

[14] J-P.E. Grolier, G.C. Benson and P. Picker, J. Chem. Thermodynamics, 7 (1975) 89.

[15] J-P.E. Grolier and A. Inglese, Can. J. Chem., 54 (1976) 1952.

[16] E. Wilhelm, Ber. Bunsenges. Phys. Chem., 81 (1977) 1150.

[17] J.B. Ott and C.J. Wormald, in K.N. Marsh and P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol IV: Solution Calorimetry, Blackwell, Oxford (1994) p. 161.

[18] X. Chen, J.L. Oscarson, H. Cao, S.E. Gillespie and R.M. Izatt, Thermochim. Acta, 285 (1996) 11.

[19] J-P.E. Grolier, Pure Appl. Chem., 62 (1990) 2115.

[20] M. Baba, L. Dordain, J-Y. Coxam and J-P.E. Grolier, Ind. J. Techn., 30 (1992) 553.

[21] C. Mathonat, V. Hynek, V. Majer and J-P.E. Grolier, J. Solution Chem., 23 (1944) 1161.

[22] C. Mathonat, Ph.D. Thesis, University Blaise Pascal, Clermont-Ferrand, France (1995).

[23] C. Mathonat, V. Majer, A.E. Mather and J-P.E. Grolier, submitted for publication.

[24] S. Degrange, V. Hynek, V. Majer and J.R. Quint, 51st Calorimetry Conference, Paper No. 59, Vancouver, Canada, 4-9 August 1996; V. Hynek, S. Degrange, M. Polednicek, V. Majer, J.R. Quint, J-Y. Coxam and J-P.E. Grolier, Symposium on Thermal Analysis in Industry and Research, Freiburg, Germany, 24–26 September 1996.

[25] V. Hynek, M. Obsil, V. Majer, J.R. Quint and J-P.E. Grolier, Int. J. Thermophys, 18 (1997) 719.

[26] P. Picker, P-A. Leduc, P.A. Philip and J.E. Desnoyers, J. Chem. Thermodyn., 3 (1971) 631.

[27] J.P.E. Grolier, G.C. Benson and P. Picker, J. Chem. Eng. Data, 20 (1975) 243.

[28] A. Inglese, E. Wilhelm and J-P.E. Grolier, 37th Annual Calorimeter Conference, Paper No. 54, Snowbird UT, 21–23 July, 1982; J-P.E. Grolier, A. Inglese and E. Wilhelm, J. Chem. Thermodyn., 16 (1984) 67.

[29] M.E. Saint-Victor and D. Patterson, Fluid Phase Equil., 35 (1987) 237.

[30] J-P.E. Grolier and G.C. Benson, Can. J. Chem., 62 (1984) 949.

[31] A. Lainez, G. Roux-Desgranges, J-P.E. Grolier and E Wilhelm, Fluid Phase Equil., 20 (1985) 47.

[32] A. Lainez, J-P.E. Grolier and E. Wilhelm, Thermochim. Acta, 91 (1985) 243.

[33] A. Lainez, E. Wilhelm, G. Roux-Desgranges and J-P.E. Grolier, J. Chem. Thermodyn., 17 (1985) 1153.

[34] E. Jimenez, L. Romani, M.I. Paz Andrade, G. Roux-Desgranges and J-P.E. Grolier, J. Solution Chem., 15 (1986) 879.

[35] M. Pintos, R. Bravo, M.C. Baluja, M.I. Paz Andrade, G. Roux-Desgranges and J-P.E. Grolier, Can. J. Chem., 66 (1988) 1179.

[36] R.G. Rubio, M. Caceres, R.M. Masegosa, L. Andreolli-Ball, M. Costas and D. Patterson, Ber. Bunsenges. Phys. Chem., 93 (1989) 48.

[37] L. Andreolli-Ball, M. Costas, D. Patterson, R.G. Rubio, R.M. Masegosa and M. Caceres, Ber. Bunsenges. Phys. Chem., 93 (1989) 882.

[38] A. Lainez, M.R. Lopez, M. Caceres, J. Nunez, R.G. Rubio, J-P.E. Grolier and E. Wilhelm, Trans. Farad. Soc., 91 (1995) 1941.

[39] R.H. Wood and D. Smith-Magowan, in S.A. Newman (Ed.), Thermodynamics of Aqueous Solutions with Industrial Applications, ACS Symposium Series 133, Washington D.C (1980) 569.

[40] D. Smith-Magowan and R.H. Wood, J. Chem. Thermodyn., 13 (1981) 1047.

[41] J-P.E. Grolier, in K.N. Marsh and P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol IV: Solution Calorimetry, Blackwell, Oxford (1994) 43.

[42] J.A. Gates, R.H. Wood, J.C. Cobos, C. Casanova, A.H. Roux, G. Roux-Desgranges and J-P.E. Grolier, Fluid Phase Equilibria, 27 (1986) 137.

[43] J-P.E. Grolier and E. Wilhelm, Pure Appl. Chem., 63 (1991) 1427.

[44] J.C. Cobos, I. Garcia, C. Casanova, A.H. Roux, G. Roux-Desgranges and J-P.E. Grolier, Fluid Phase Equilibria, 69 (1991) 223.

[45] J-Y. Coxam, J.R. Quint and J-P.E. Grolier, J. Chem. Thermodyn., 23 (1991) 1075.

[46] J-Y. Coxam, J.R. Quint and J-P.E. Grolier, High Temperatures-High Pressures, 23 (1991) 575.

[47] L. Dordain, J-Y. Coxam and J-P.E. Grolier, Rev. Sci. Instrum., 65 (1994) 3263.

[48] L. Dordain, J-Y. Coxam, J.R. Quint, J-P.E. Grolier, E.W Lemmon and S.G. Penoncello, J. Supercritical Fluids, 8 (1995) 228.

[49] S.L. Randzio, in K.N. Marsh and P.A.G. O'Hare (Eds.), Experimental Thermodynamics, Vol IV: Solution Calorimetry, Blackwell, Oxford (1994) 303.

[50] S.L. Randzio, Thermochim. Acta, 89 (1985) 215.

[51] L. Ter Minassian and Ph. Pruzan, J. Chem. Thermodyn., 9 (1977) 375.
[52] L. Ter Minassian and F. Milliou, J. Phys. E, 16 (1983) 450.
[53] S.L. Randzio, J. Phys. E, 16 (1983) 691.
[54] S.L. Randzio, J. Phys. E, 17 (1984) 1058.
[55] S.L. Randzio, D.J. Eatough, E.A. Lewis and L.D. Hansen, J. Chem. Thermodyn., 20 (1988) 937.
[56] S.L. Randzio, J-P.E. Grolier and J.R. Quint, Rev. Sci. Instrum., 65 (1994) 960.
[57] 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.
[58] S.L. Randzio, J-P.E. Grolier and J.R. Quint, Fluid Phase Equil., 110 (1995) 341.
[59] S.L. Randzio, J-P.E. Grolier and J.R. Quint, Int. J. Thermophysics, 18 (1997) 733.
[60] J-P.E. Grolier and S.L. Randzio, Fluid Phase Equil (in press).
[61] S.L. Randzio, J-P.E. Grolier and J.R. Quint, High Temperatures-High Pressures (in press).
[62] S.L. Randzio, J-P.E. Grolier, I. Zaslona and J.R. Quint, Patent No. 9109227, France; Patent No. P-295285, Poland.
[63] 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.
[64] S.L. Randzio and J-P.E. Grolier, submitted for publication.