From simple fluids to polymers, recent developments of calorimetric techniques and their contribution to thermodynamics

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Abstract: Calorimetric techniques have been developed to work with gases, pure liquids or fluid mixtures, as well as polymers. Calorimeters for measuring heat capacities have served to study gaseous systems and nonelectrolyte mixtures. Calorimeters for measuring heats of mixing have been used to investigate absorption of gases in liquids and molecular interactions in nonelectrolyte mixtures. A pressure scanning calorimeter, operated as a pVT-calorimeter, has been used to obtain from the isobaric thermal expansivity, measured over extended ranges of T and p , the full thermodynamic description of fluids from saturation pressure up to the critical region. This calorimeter has also been employed to investigate the thermomechanical behaviour of polyethylenes in the crystalline state up to 200 MPa. Typical results on selected systems illustrate the importance of accurate calorimetric data for full and precise thermodynamic description of molecular interactions, phase equilibria and materials.

INTRODUCTION

In the last two decades chemical thermodynamics has witnessed impressive advances particularly in fields of interest for materials science and chemical engineers. Constant progresses have been made concomitantly on both the experimental and the fundamental aspects nourishing in fact each other from new techniques and improved modelling. Theoretical models based on molecular interactions and taking into account thermophysical properties have become more precise and powerful, thanks to the availability of a wealth of accurate original experimental data. In this context calorimetry and associated techniques have played a decisive role. New concepts and novel designs of instruments have focused on widening the ranges of temperature and pressure. Also, significantly improved experimental precision has been obtained together with simplified, *e.g.* as much as possible automated and faster, procedures of data acquisition. From this point of view calorimetry must be regarded as a modern and major technique not only for chemical thermodynamics but for physical chemistry at large; the data and quantitative information it provides at the energy level are unique. Sophisticated instrumentation is now available for the determination of heat capacities over extended temperature and pressure ranges; this is the same for heats of mixing and pVT-measurements. A review of the state-of-the-art in solution calorimetry has appeared in 1994 in a contributing book (ref. 1) published under the auspices of IUPAC Commission I.2 on Thermodynamics.

The most recent and relevant advances we have made are illustrated with typical examples which, interestingly, concern fluids, gases or liquids, pure substances or mixtures, and polymers.

HEAT CAPACITIES OF LIQUIDS AND GASES

Dealing with organic liquid mixtures at 298.15 K and atmospheric pressure, the main progress has been in the systematic use of heat capacities, measured with a Picker-type flow microcalorimeter, to correlate and/or predict all excess properties in different classes of systems (refs. 2-3). This was done using group contribution methods allowing then a strict comparison between UNIFAC (Dortmund) (ref. 4) and DISQUAC (ref. 5) models. To illustrate the use of experimental data, *e.g.* the importance of heat capacities, we have selected mixtures containing the ester and the aromatic groups which are of interest in polymers science. Experimental data on excess molar Gibbs energies G^E, enthalpies H^E, and heat capacities Cp^E, have been collected for binary systems n-alkylalkanoates + toluene. Numerical comparison of experimental data with DISQUAC and UNIFAC (Dortmund) calculations are given in Table 1. As expected the two models reproduce fairly well the G^E-data, agreement being less satisfactory for H^E-data. But clearly, Cp^E-data constitute a severe test for theoretical models in showing that DISQUAC has a better capacity to represent and predict these excess properties, whereas UNIFAC gives values which may depart greatly from experimental results.

TABLE 1. Excess molar quantities of binary mixtures n-alkylalkanoates + toluene at different temperatures T and equimolar fraction x. Comparison of experimenal results (exp.) with values calculated by DISQUAC (Disq.) and UNIFAC (Dortmund) (Unif.).

n-alkylalkanoates	T,K	exp.	Disq.	Unif.	Source of data
			G^E, J mol^{-1}		
HCOOC$_2$H$_5$	318.15	332	320	326	Ohta et al, 1983 (ref. 6)
	321.15	321	318	328	Macedo et al, 1984 (ref. 7)
	325.15	333	317	331	Macedo et al, 1984 (ref. 7)
C$_2$H$_5$COOCH$_3$	298.15	142	145	233	Borchardt et al, 1981 (ref. 8)
			H^E, J mol^{-1}		
HCOOC$_3$H$_7$	298.15	184	189	53	Delcros et al, 1995 (ref. 2)
HCOOC$_4$H$_9$	298.15	96	95	-2	Delcros et al, 1995 (ref. 2)
CH$_3$COOC$_2$H$_5$	298.15	90	90	97	Delcros et al, 1995 (ref. 2)
	298.06	93	91	97	Gmehling and Meents, 1992 (ref. 9)
	343.15	100	97	291	Gmehling and Meents, 1992 (ref. 9)
CH$_3$COOC$_3$H$_7$	298.15	-29	-37	-48	Delcros et al, 1995 (ref. 2)
CH$_3$COOC$_4$H$_9$	298.15	-105	-109	-138	Delcros et al, 1995 (ref. 2)
			Cp^E, JK^{-1}mol^{-1}		
HCOOC$_3$H$_7$	298.15	0.490	0.550	-1.734	Jiménez et al, 1994 (ref. 10)
HCOOC$_4$H$_9$	298.15	0.217	0.140	-1.882	Jiménez et al, 1994 (ref. 10)
CH$_3$COOC$_2$H$_5$	298.15	-0.007	0.036	5.921	Jiménez et al, 1994 (ref. 10)
CH$_3$COOC$_3$H$_7$	298.15	0.506	0.515	5.884	Jiménez et al, 1994 (ref. 10)
CH$_3$COOC$_4$H$_9$	298.15	0.203	0.297	5.746	Jiménez et al, 1994 (ref. 10)
C$_2$H$_5$COOCH$_3$	298.15	0.103	0.007	5.479	Jiménez et al, 1994 (ref. 10)
C$_2$H$_5$COOC$_2$H$_5$	298.15	0.067	0.039	5.334	Jiménez et al, 1994 (ref. 10)
C$_2$H$_5$COOC$_3$H$_7$	298.15	0.553	0.558	5.166	Jiménez et al, 1994 (ref. 10)

In order to extend the p and T ranges of heat capacity measurements we decided to favoured techniques using a differential heat flux detector based on the Calvet principle. We have thus developed an experimental method for measuring heat capacities of gases. The central part of the instrument is a C80 D-Setaram calorimeter, in which high pressure cells have been adapted. An initial version (ref. 11) of the set-

up had been designed to study aqueous electrolyte solutions (ref. 12) up to 550 K and 20 MPa. A more recent version, as shown on Fig. 1, has been described in details elsewhere (ref. 13). Two cylindrical cells (inner volume $\approx$ 11 cm^3) made of stainless steel, were specially designed to sustain temperatures up to 573 K and pressures up to 30 MPa. The temperature is read to $\pm$ 0.06 K by means of a 100 Ω platinum resistance, located between the two cells. The temperature of the block can be varied with a maximum rate of 0.1 K s^{-1}. Since the operation of the instrument is made in the static mode (no fluid circulating through the instrument) heat leaks by conduction and connection through the cells connecting tubes had to be eliminated. A better temperature control was obtained through the adjunction of an additional thermostat
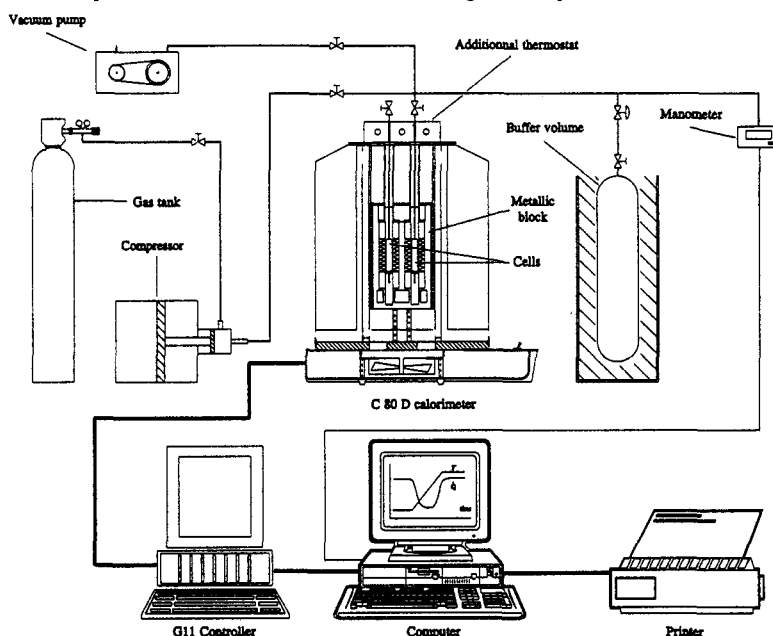

Fig. 1 Schematic diagram of the heat capacity set-up with peripheral instrumentation.

on the top (the "head") of the calorimeter (see Fig. 1); additional thermal guards around the connecting tubes further improved the temperature control of the cells. 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 liter cylinders connected together and placed inside a cylindrical thermostatted block. With this arrangement, the pressure inside the cell can be read with an accuracy of 0.5 % of the full scale of a 50 MPa pressure gauge. A computer is used to monitor the whole set-up through a RS-232 interface; a typical constant pressure experiment covering the temperature range from 323 to 423 K can be run fully automated in 24 hours.

Having heats capacities over ranges of p and T makes possible to represent most of the thermodynamic characteristics of a fluid. In this respect heat capacities can be used either to develop new equations of state or to check the validity of existing equations. This is well illustrated with experimental heat capacities of carbon dioxide measured slightly above the critical point and of argon measured well above the critical point (ref. 14); they agree within 1.5 % with the values calculated using the equations of state of Ely et al. (ref. 15) and of Stewart and Jacobsen (ref. 16) respectively. This excellent agreement between directly measured heat capacities and equation of state calculations is further observed for gaseous mixtures used as natural gas models. Typically, for a given "synthetic" natural gas (composition in moles per cent : CH_4, 83.427; C_2H_6, 3.548 ; C_3H_8, 0.871 ; N_2, 10.619 ; CO_2, 1.535) the absolute deviations between experimental data and values calculated using various equations of state allow to critically assess the quality of available equations of state (refs. 17-18). As shown on Fig. 2 most of the current equations of state, *e.g.* Soave, Peng-Robinson (P.R), Lee-Kesler (L.K), Simonet-Behar-Rauzy (S-B-R) and American Gas, Association 1988 (AGA 8) can be used to calculated heat capacities over a large range of temperatures to better than $\pm$ 2 %, contrary to the chain-of-rotations (C-O-R) which yields heat capacities to not better than 4-7 %.
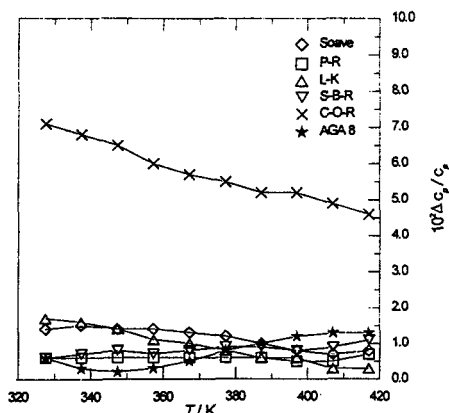
Fig. 2 Absolute average deviations, 10^2 $\Delta Cp/Cp$, between experiments and equations of state, over the temperature range 320-420 K, for a "synthetic" natural gas (see text).

Undoubtedly equations of state exist which can calculate heat capacities of gases quite reliably, questioning therefore the experimental efforts to get these properties. Nevertheless, precise experimental data must be available to make a screening of the performances of theoretical models.

HEATS OF MIXING OF FLUIDS

Our long time involvement in heat of mixing calorimetry has its origin in the direct study of molecular interactions by modelling heat effects, as a matter of fact, excess enthalpies obtained by mixing substances of different classes; the aim being to selectively characterise the pair-interchange energies between chemical groups. A systematic study of organic mixtures has led to a vast database of heat capacities and of heats of mixing which has been used to elaborate consistant group contribution models (see for example, refs. 2-3, 5 and refs. therein). Extending the prediction capability of such models to higher temperatures and pressures was surely the driving force to design mixing calorimeters able to work at superambient conditions. Here again, detectors based on the Calvet principle were used to measure heats of mixing under flow conditions up to 573 K and 40 MPa (ref. 19). An elaborated and more sophisticated version of such calorimeter, recently described in details (ref. 20), has been used in two directions.

Firstly, the investigation of aqueous organic systems has consisted in pushing away the temperature and pressure limits of solubilisation of organic substances in water in connection with the removal of organic pollutants, using hot water. Figure 3 shows examples of the possibilities of the calorimeter : the excess enthalpies of mixing for the systems ethanol + H_2O (ref. 20) and benzene + H_2O (ref. 21) respectively, at elevated temperatures and pressures.

Secondly, the investigation of the absorption of acidic gases in aqueous mixed "physico-chemical solvents" has consisted in determining two essential quantities for the elimination of such gases. This is well illustrated on Fig. 4; from the appropriate plot of the measured enthalpy as a function of the acidic gas loading one can easily obtain the heat of absorption of the gas in the given solvent as well as the corresponding solubility limit.

We have recently shown that the CO_2 solubilities obtained either indirectly by calorimetry or by direct solubility measurements agree reasonably well (refs. 22a and b).
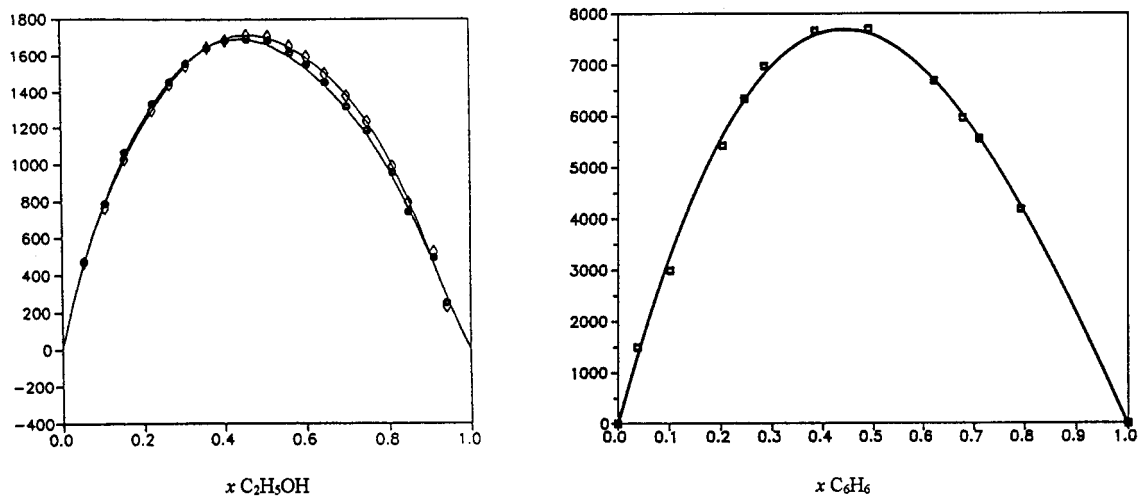
Fig. 3 Excess molar enthalpies H^E in J mol^{-1} versus the mole fraction x: (left) for C_2H_5OH + H_2O at 523 K and two pressures ◊, 15 MPa ; •, 20 MPa ; (right) for C_6H_6 + H_2O at 563 K and one pressure □, 17.5 MPa.
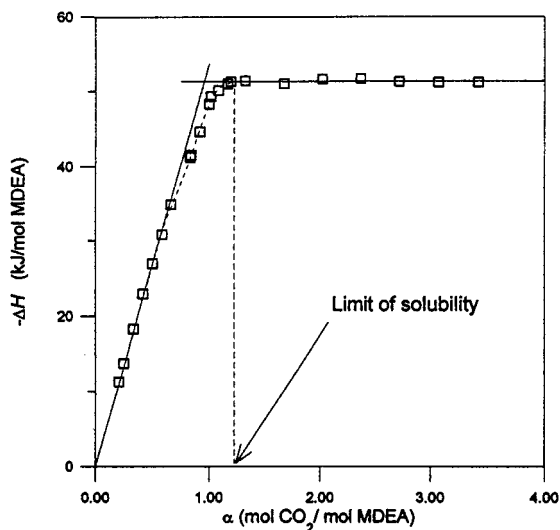

Fig. 4 Absorption of CO_2 in a 30 wt % aqueous solution of methyldiethanolamine (MDEA) at 313.15 K and 2.0 MPa. Enthalpy versus CO_2 loading α (mol CO_2/mol MDEA); with indication of the saturation loading point.

An ultimate and very promising new version of a heat of mixing calorimeter has just been completed It features in fact a "calo-densitometer" operated in the dynamic flow mode (refs. 23a and b) in which the liquid system to study is formed upon mixing in the "hot zone" of the calorimeter, where the enthalpy of mixing is measured, then circulated to the flow densitometer connected in series, where the density is measured on the same sample under the same conditions of T and p. With this instrument a large number of systems which otherwise could not be efficiently investigated are now possible to consider; furthermore, by combination of the quantities then obtained, Henry's constants, activity coefficients, *e.g. pVT*-properties, will be readily available.

PRESSURE CONTROLLED CALORIMETRY FOR FLUIDS AND POLYMERS

Since its introduction in the late eighties by Randzio et al (ref. 24), pressure controlled calorimetry has open a new era in thermodynamics, with many potential applications not yet touched. As a matter of fact, it is truly *pVT*-calorimetry, making use of the Maxwell relations, where one of the state variables is scanned while another is kept constant. The output is always a thermal effect resulting from the change of the variable, together with a mechanical coefficient of the sample under investigation, over extended ranges of temperatures and pressures. Three complete set-ups exist at three different locations (Brigham University, Provo, Utah; Institute of Physical Chemistry, Warsaw, Poland; Blaise Pascal University, Clermont-Ferrand, France) which are operated in a concerted international cooperation. Illustrative examples are taken from the work carried out at Blaise Pascal University. The instrument patented in both France and Poland and recently described in details (ref. 25) makes use of a Setaram C80-calorimeter to which a pressure scanning device and high pressure cells have been adapted. The isothermal calorimeter is controlled by linear pressure variations in the range 0.1-400 MPa at temperatures from 303 to 573 K. The rate of pressure variations can be as low as 0.002 MPa s^{-1} over the entire pressure range. When the temperature T is kept constant and the pressure is varied as a linear function of time, the power, *e.g.* the energy change detected by the calorimeter, is given by relation (1)

$$P_T(p) = - (\pm \alpha_s V_{in} T a) \qquad (1)$$

where α_s is the isobaric coefficient of thermal expansion of the substance under investigation; V_{in} being the internal calorimeter cell volume and a the pressure scanning rate. One of the most comprehensive investigations using the set-up concerned n-hexane as a model for compressed simple liquids (ref. 26). The isobaric thermal expansivities α_p measured from just above the saturation vapor pressure to 40 MPa at temperatures from 303 to 453 K and to 300 MPa at 503 K were used to obtain a correlation equation for α_p valid from 240 to 503 K at pressures up to 700 MPa; from this equation several important thermophysical quantities could be deduced. A striking feature of these results is the single crossing point around 80 MPa observed for the α_p-isotherms plotted against pressure. This singular point is considered now as a characteristic point to be used as a standard test for equations of state of dense fluids (refs. 27-28). More recently we shown (ref. 29) in the case of 1-hexanol, that such a single crossing point is shifted to higher pressures (above 200 MPa) for associated liquids. A study of binary mixtures 1-hexanol + n-hexane has allowed to systematically investigate (ref. 30) the pressure and temperature derivatives of the main excess thermodynamic quantities as shown in the case of G^E on Fig. 5. These derivatives are essential to further develop theories of nonelectrolyte mixtures.
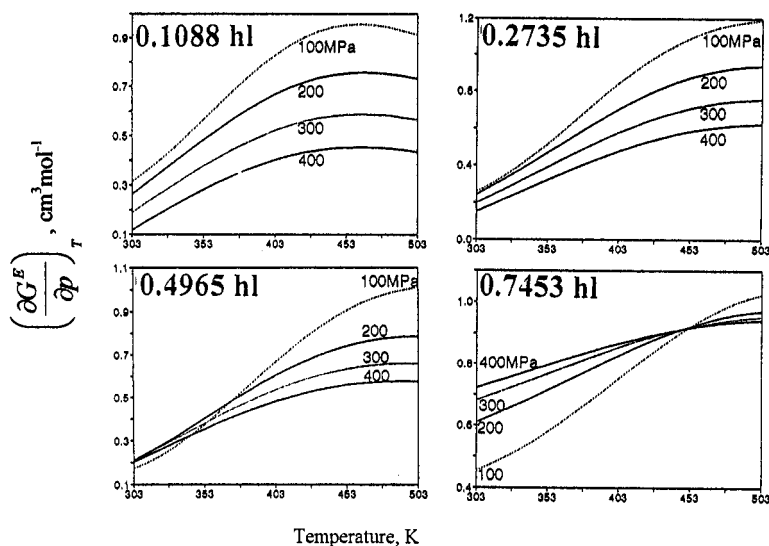

Fig. 5 Binary mixtures hexanol + n-hexane. Examples of excess function derivatives with respect to p, plotted against T(K), for different hexanol (hl) mole fractions (0.1088, 0.2735, 0.4965 and 0.7453); $(\partial G^E /\partial p)_T = V^E$ (cm^3 mol^{-1}).

When dealing with polymers, the pressure scanning calorimeter is advantageously named "transitiometer". In that case pressure controlled calorimetry is used to investigate the changes undergone by polymeric materials when submitted to temperature or pressure variations. Typically glass transitions and fusion/solidification can be easily investigated. In addition, the hydraulic fluid transmitting the pressure to the sample can be selected. With non-reacting mercury normally used, phase transitions of pure materials are accessible; when a gas replaces mercury, solubility and reaction may occur with the sample which modify the phase transition. Moreover, the thermal effect associated with the absorption of the gas in the polymer can be measured. In the last few years, we have favoured transitiometric studies of various polymers submitted to temperature, pressure and/or chemical stress (ref. 31). Considering pure polyethylenes, a typical result is the linear dependence with crystallinity of the isobaric thermal expansivities α_p (ref. 32). Another interesting observation is the good agreement of our results for α_p with the values calculated using the equation of state of Pastine, developed from crystallographic data (ref. 32). A final illustrative example is taken from an outgoing research project dealing with high pressure gas solubilities in polymers. A careful study of polyethylenes reacting with supercritical methane have shown that the higher the gas pressure at fusion the lower is the temperature of fusion. Moreover, permanent and stable, but reversible, "changes" can be induced in the material "organisation". In the field of polymers science results obtained from transitiometry are surely broadening the domain of theoretical developments.

CONCLUSION

Calorimetric techniques very versatile in terms of energetic effects measured and of nature of the samples possible to investigate (gases, liquids, solids) can be used over extended temperature and pressure ranges. Precision measurements and automated operations make them real physico-chemical techniques to be used in many fields of applied and fundamental interests. Recent experimental designs are providing new data which induce advanced theoretical developments. In addition, novel experimental techniques such ap pVT-calorimeters are suitable educational tools for practical thermodynamics teaching.

ACKNOWLEDGEMENTS

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