Solution calorimetry at high temperatures and elevated pressures

Jean-Pierre E. Grolier

Laboratoire de Thermodynamique et Cinétique Chimique, Université Blaise Pascal
Clermont-Ferrand, 63177 Aubière, France

Abstract. To study solubility phenomena several calorimetric
techniques can be used to deliver high precision data which allow a
complete thermodynamic description of the phase behavior of a liquid
system in the pressure interval 0.1-500 MPa and at temperatures up
to 570 K.

INTRODUCTION

Solubility phenomena are quantitatively investigated by a thermodynamic approach. This
implies the complementary use of both rigorous relations between pertinent variables and
precision methods for the determination of solubility data. The quantitative investigation
of the solubility of gases in liquids is by far the most accomplished example of this
approach, which is best illustrated by a recent well documented review by Wilhelm (ref. 1).
Correlation and prediction of solubility phenomena through model calculations are only
possible when using reliable experimental data. In this respect, among the traditional or
conventional experimental techniques of physical chemistry calorimetry appears as a major
technique in the sense that it can deliver directly some of the key relevant thermodynamic
variables. Typically, at room temperature and atmospheric pressure, calorimetric techniques
have been successfully used to understand and characterize solubilization processes in
various cases. Again the best example is the solubility of gases in liquids where excellent
agreement is shown by enthalpies of solution obtained either by direct calorimetric methods
(refs. 2-4) or by direct gas solubility measurements (ref. 5-7). Also under normal
conditions of temperature and pressure calorimetry, by means of heat capacities, is
currently used to characterize molecular interactions which are responsible for the
solubilization pattern in various mediums. This includes binary mixtures where complex
formation between polar substances takes place (refs. 8-10), binary mixtures of a polar
substance with an n-alkane near the UCST (ref. 11) or multicomponent aqueous systems
containing surfactants (ref. 12 and references therein). In this context an extensive study
of mutual solubility between alkanes and alkanols has been carried out looking at the
influence of self-association in an aliphatic medium depending upon the length of both the
alkane or the alkanol, particularly near infinite dilution of the alkanol (ref. 13).

Such accumulation of new data in many different areas has brought an original vision of
solutions with new insight into the liquid state. This situation results from rapid recent
progress in the determination of heat capacities of liquids. As a matter of fact we are
witnessing an impressive growth in the field of experimental calorimetry which, associated
will the relevant thermodynamic relations allows a deep thermodynamic description of
equilibrium phenomena in liquid solutions over wide ranges of temperature and pressure. In
what follows the thermodynamic procedure and pertinent fundamental relations are presented
together with the new developments in experimental techniques which can provide the key data
for the above description. This survey is mainly based on the work done at the University
Blaise Pascal.

THERMODYNAMIC FUNDAMENTALS AND CALORIMETRIC DATA NEEDS

For mixtures the importance of the molar excess enthalpy h^E which is identical to the heat
of mixing at constant pressure P is well known. First as a deviation from ideal behavior
requiring theoretical explanation it has a fundamental importance. Second as a measure of the
thermal effect during a mixing process it has a practical importance. At least three major
publications or reference books (ref. 14) attest to the importance of h^E as primary data.

As the first derivative with respect to temperature T, of h and the second derivative of
the Gibbs free energy g (or μ), the heat capacity at constant pressure c_p is of particular
interest. This quantity, very sensitive to molecular interactions, can be used to study

phenomena at a molecular level, and its direct measurement is also of a major importance from both fundamental and practical points of view. Thus by virtue of the basic relations

$$c_p = (\partial h/\partial T)_p = T(\partial s/\partial T)_p = -T(\partial^2 g/\partial T^2)_p \qquad (1)$$

c_p brings valuable information on the main thermodynamic functions, considering also the entropy s.

If we introduce the mechanical coefficients $\alpha_p = \frac{1}{v}(\partial v/\partial T)_p$ (isobaric expansivity), $\beta_T = \frac{1}{v}(\partial v/\partial P)_T$ (isothermal compressibility) or $\beta_s = -(\partial v/\partial P)s$ (isentropic compressibility) we easily get the simple relations (including the heat capacity at constant volume c_v, M being the molar mass)

$$c_p/c_v = \beta_T/\beta_s = 1 + TM\,\alpha_p^2/\beta_s c_p \qquad (2)$$

$$c_p - c_v = Tv\,\alpha_p^2/\beta_T \qquad (3)$$

$$\beta_T - \beta_s = T\alpha_p^2/c_p \qquad (4)$$

By appropriate derivations we obtain the most important relations for describing the changes of the thermodynamic functions over the whole pressure and temperature ranges

$$(\partial c_p/\partial P)_T = -T(\partial^2 v/\partial T^2)_p = -Tv\left[\alpha_p^2 + (\partial\alpha_p/\partial T)_p\right] \qquad (5)$$

and also

$$(\partial\alpha_p/\partial P)_T = -(\partial\beta_T/\partial T)_p \qquad (6)$$

Besides the quantity β_s which is currently obtained from experimentally measured speed of sound ω through $\beta_s = v/M\,\omega^2$, the other fundamental quantities namely c_p, β_T, α_p can now be obtained for any liquid (pure or mixed) by direct precise calorimetry measurements. As for the excess enthalpy h^E, the experimental quantity of interest when dealing with mixtures or solutions, it is also obtained by direct calorimetry. The subsequent paragraphs is give a survey of the calorimetric techniques recently developed to obtained the above four quantities h^E, c_p, β_T and α_p. Emphasis is placed on the potential for these techniques to deliver high T and high P data.

DETERMINATION OF HEATS OF MIXING BY FLOW CALORIMETRY

After the pioneering work of Wadsö (ref. 15) and Picker (refs. 16-17) in the late sixties flow calorimetry, better designated by concentration scanning calorimetry, has imposed itself as the best method to measure h^E. As regards high temperature and high pressure measurements our own work in this domain has been largely inspired by that of Christensen et al. (refs. 18,19), of Busey et al. (ref. 20) and of Randzio and Tomaszkiewicz (refs. 21-23). The calorimeter which has been built (ref. 24) at the Laboratory of Thermodynamics and Chemical Kinetics in Clermont-Ferrand features active heat echange to bring the liquids to be mixed to the working temperature, and the use of a Calvet type differential heat flux detector. Two identical cells (Fig. 1), made of hastelloy are fitted to the detector of a C 80 Setaram calorimeter. Before entering the mixing cell the liquids are circulating in a preheater/heat exchanger compartment. This design allows constant temperature adjustment of the incoming liquids to the temperature of the mixing cell. The flow controlling system consists of a double syringe metering pump (Brownlee Microfeed Pump).

The pressure control in the whole liquid line is assured by means of a back pressure regulator (spring loaded model 155 from Grove at low pressure or pressurized dome Circle Seal model BPR 21 at elevated pressure). Both the Brownlee pump and the back pressure regulator can be operated with either gases or liquids which permits the calorimetric setup to be used to measure liquid/liquid as well as gas/liquid systems. In the latter case when measuring the heat of mixing (or heat of dissolution) of a gas in a liquid we can get directly the heat itself at as well as the solubility limit concentration indicated by a break point on the heat of mixing curve versus concentration (gas mole fraction for example). To test the performance of the whole calorimetric arrangement the system CO_2 + hexane has been used and check measurements have been made against the results of Christensen et al. Presently this calorimetric setup can be operated up to 570 K and 30 MPa.

DETERMINATION OF HEAT CAPACITIES

Two different calorimeters are currently in operation in the Laboratory of Thermodynamics and Chemical Kinetics. Both use the Calvet type differential detection of the heat flux from
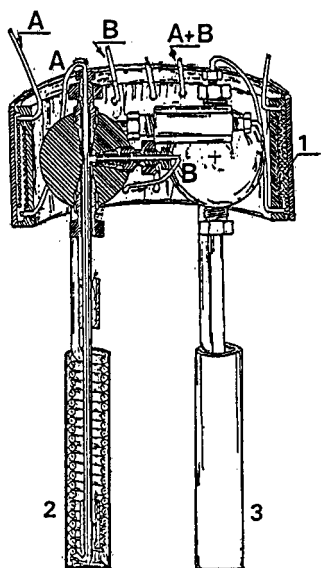
Fig. 1.
View of the high pressure and
elevated temperature heat of
mixing calorimeter :
1, preheater/heat exchanger
with thermocoax for active
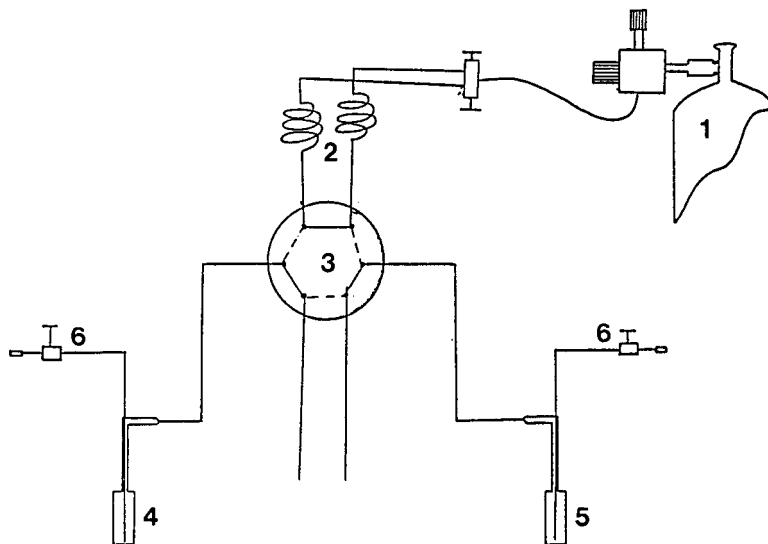regulation ; 2, mixing cell ;
3, reference cell.

Fig. 2.
Scheme of the arrangement used for measuring heat capacities
under pressure : 1, nitrogen cylinder ; 2, pressure regulator ;
3, Rheodyne valve ; 4, measuring cell ; 5, reference cell ;
6, valve and filling port for each individual cell.

the measuring cell against the heat flux from the reference cell. Between 275 and 375 K, at
atmospheric pressure, we use a new temperature scanning calorimeter (Setaram micro DSC)
previously described (ref. 25). The main characteristics of this instrument are the small
volume (1 cm^3) of the cells and the use of a liquid thermostat to ensure the thermal
equilibrium of the detection block. The temperature of this block, which contains the
measuring and reference cells, can be programmed linearly both on heating and cooling. In
the temperature range 275-375 K precise measurements can be performed at preestablished
temperatures. For this at each of the preestablished temperatures a temperature increment ΔT
is used to detect the difference in heat capacity between the reference and sample liquids.
All the operations such as temperature scanning and ΔT production are entirely computer
controlled and the volumetric heat capacities, c_p/v, are obtained with precision of ± 1 x 10
J.K^{-1}.cm^{-3}.

Between 300 and 570 K we use a Setaram C 80 calorimeter in which we have adapted (ref. 26)
two identical cells (8 cm^3 internal volume) made of hastelloy C 276 and working up to 30 MPa
(Fig. 2). The main difference with the micro-DSC concerns the temperature control of the
block containing the cells. Instead of a liquid thermostat a heater brings the temperature
of the block up to the working value thus measurements are only possible upon heating. The
pressure inside the cells is held constant at the desired value through the use of a
nitrogen cylinder, a pressure regulator and a high pressure valve (Rheodyne) as illustrated
Fig. 2. In this way the pressure, can be read with a digital Heise gauge to ± 0.1MPa. The
practical method used to obtain the volumetric heat capacity $(c_p/v)_x$ of solution x against
the value $(c_p/v)_{H_2O}$ of water has been refined in order to get the best precision while
keeping the shortest measuring time. The method consists in obtaining $(c_p/v)_x$ between to
temperatures T_i et T_f (of the ΔT increment) by use of the relation (ref. 26)

$$\int_{T_i}^{T_f} (c_p/v)_x \, dT = \frac{S(x, empty) - S(empty, empty)}{S(H_2O, empty) - S(H_2O, H_2O)} \int_{T_i}^{T_f} (c_p/v)_{H_2O} \, dT \qquad (7)$$

where S(a,b) represents the heat flux differences measured between cell a (measure) and cell
b (reference) depending on their respective contents. The times necessary for the initial
thermal equilibrium and to return to equilibrium after a ΔT, that is to say in order to
establish the base lines before and after the ΔT, have been optimally reduced in such a way
that nine (c_p/v) values are obtained at nine different selected temperatures in the
calorimeter temperature range, in about 35 hours. This method is now in real competition
with the one used by Wood and collaborators (ref. 27) based on a dynamic flow calorimeter.

DETERMINATION OF EXPANSIVITY AND COMPRESSIBILITY BY
PRESSURE CONTROLLED CALORIMETRY

The pressure-controlled scanning calorimetry (PCSC) is based on using the pressure as an independent thermodynamic variable (refs. 28-29). The calorimeter which is operating at the University Blaise Pascal (ref. 30) has been built in collaboration with the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw. The schematic diagram of the experimental setup is given in Fig. 3. The thermal detector is a C80 Setaram calorimeter. The calorimetric vessels made of stainless-steel can be operated in the range 300-570 K up to 500 MPa. The programming of the pressure in the measuring and reference vessels is obtained with a special device, a digital pressure feedback to provide any time depending pressure scanning. With this technique the system can compensate automatically not only for the changes in volume due to compression or expansion but also for the changes resulting from phase transitions or chemical reactions.

The scanning of the pressure can be performed either in a static mode with a stepwise procedure or in a dynamic mode changing the pressure at a given linear low rate. The quality of the whole setup (calorimetric detector and pressure scanning device) can be judged from the agreement of the calibration constant K obtained (ref. 30) with either nitrogen or hexane as the calibrating fluid ($K_{N_2}/MPa.V.^{-1}s^{-1} = 24,61 \pm 0,35$; $K_{hexane}/MPa.V.^{-1}s^{-1} = 24,95 \pm 0,19$) in either the static or dynamic mode. This calibration constant is expressed, for a ΔP increment at a constant temperature T by

$$K = \frac{(\alpha - \alpha_{ss})\Delta P \, T}{Int} \qquad (8)$$

where α is the expansivity of the calibrating liquid, α_{ss} the expansivity of the material from which the vessel is made and Int the integral of the thermogram resulting from the calorimeter response to the pressure change ΔP. Using for example nitrogen (in the static mode) as the calibrating liquid the agreement between values of the expansibility α of hexane in the static or dynamic modes is illustrated in Fig. 4.

The system presented in Fig. 3 can be used for determination of the expansibility or of the compressibility of a fluid over a large pressure range, up to 500 MPa and at temperatures up to 570 K. The pressure change rate is typically 0.02 MPa.s^{-1} and can be as low as 0.005 MPa.s^{-1}.
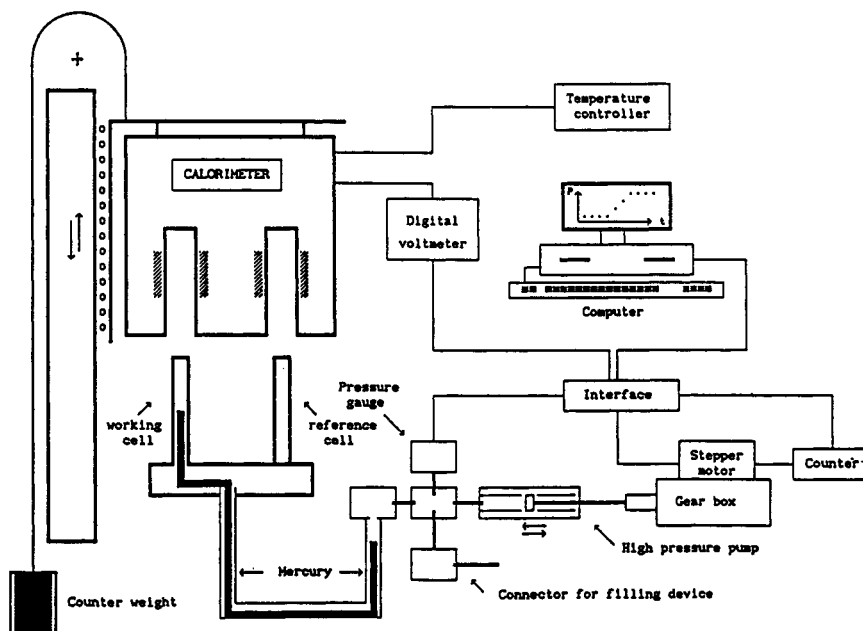

Fig. 3. Schematic diagram of the pressure controlled scanning calorimeter. The working and reference cells are maintained firmly at a fixed position and connected to the controlled pressure device. The calorimeter is inverted on a special stand so that it can be moved up and down over the calorimetric cells.
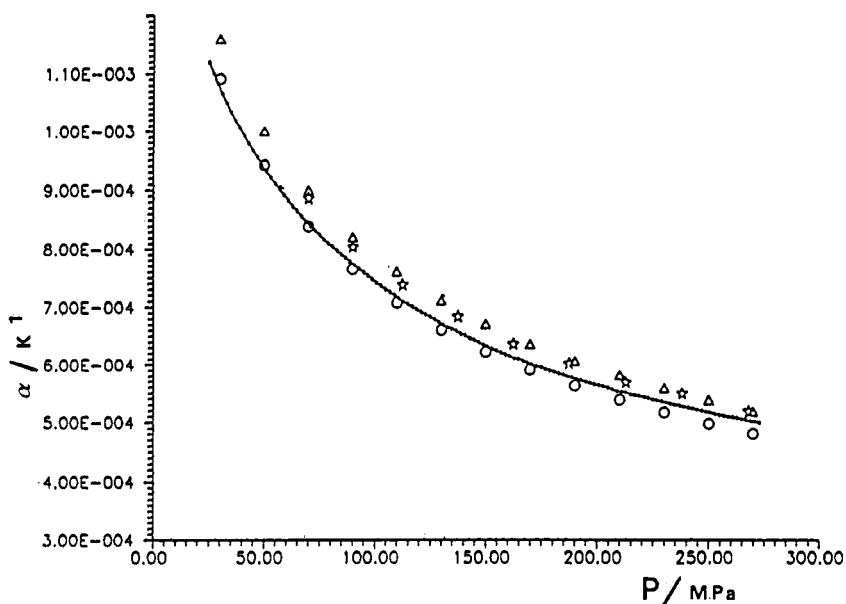
Fig. 4. Isobaric expansivity of hexane at 354.6 K obtained with the pressure controlled scanning calorimeter during a linear pressure scan (dotted continuous curve) compared to stepwise measurements the stars, ref. 30; triangles, ref. 28; open circles: ref. 31.

CONCLUSION

Thanks to recent progress in calorimetric techniques we now have at hand several powerful techniques which can be used together to provide a sound thermodynamic description of a liquid system over the pressure range 0.1 to 500 MPa at temperatures up to 570 K.

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