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HIGH PRESSURE CALORIMETRY
Comparison of two systems (differential *vs.* single cell) Application to the phase change of water under pressure

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Abstract

In high pressure calorimetry the pressure change is used to obtain the desired phenomenon (i.e. phase change) at constant temperature. Two high pressure calorimeters have been developed to measure the latent heat of fusion of pure water (hexagonal ice-type I) at subzero temperature. Both calorimeters used a constant pressurisation rate produced with a high pressure pump driven by a step motor. The first calorimeter was a single cell calorimeter where mercury acted as the pressurisation fluid, while the second one was differential (two cells) and was pressurised with pentane. Both calorimeters gave high accuracy data of latent heat of fusion of pure water, which were determined taking into account that either the fluid used to pressurise or the pressurisation rate affected the calorimetric signal.

Keywords: calorimetry, gelatine gels, high pressure, ice, phase change, water

Introduction

Calorimetry is a very versatile method to measure thermodynamic properties of substances and to follow phase change phenomena. In most applications, calorimetry is carried out at constant pressure while the tracked phenomenon is observed on increasing or decreasing the temperature (either stepwise or at a constant scanning rate) [1].

Examples of experiments carried out at constant pressure (different from atmospheric pressure) are offered by some authors [1, 2] who studied the influence this state variable on the thermodynamic properties. Most of the researchers worked in isothermal conditions and changed pressure step by step [3] or at a constant rate [4]. Some alternative techniques [5, 6] based on the volume variation produced by varying the pressure in isothermal conditions allowed estimation of the latent heat of fusion of water [6] and mercury [5] *via* the Clapeyron equation. Other researchers [7] developed a novel piezometer to measure the thermophysical properties of a magnesium sulfate aqueous solution undergoing phase transition. [8–10] were able to measure the thermal expansivity

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and the isothermal compressibility of selected liquids by using a method based on the measurement of the heat of compression of the sample subjected to a step pressure evolution. Original results were obtained with different alkane such as hexadecane, butane-1,4-diol [11], *n*-alkanes C_{21}, C_{23} and C_{25} [12], carbone tetrachloride [3] and benzene [3, 13]. This technique found followers in different research domains like planetology: the behaviour of magnesium-sulfate aqueous solution at low temperature was studied at low temperature for planetology applications [7].

High pressure calorimetry requires pressure resistant and heavy cells. This implies a limitation in the fine control of temperature changes. This is why pressure changes are produced in isothermal conditions. Another problem to face concerns the pressure transmitting medium which necessarily flows through the cell. Two different principles have been used, namely, constant mass or constant volume. Most of the studies available in literature are related to liquids and used the constant volume technique. The studied liquid was then used as the pressure transmitting fluid. Single cell calorimeters were used in most cases, the heat dissipated by the cell being subtracted from the overall calorimetric signal [11] to evaluate the contribution from the sample. The constant mass approach can instead be used for solid materials. It was presented by some authors [4, 14, 15], one of whom used mercury as a pressurisation fluid and installed the liquid to be studied above the mercury level (the sample was then ‘floating’ above the mercury, beneath the obturator of the cell. A differential system was used.) Chourot [14] developed a single cell system to measure the latent heat of fusion of pure water and aqueous solutions of $MgSO_4$ (mass/mass) and KCl [15] at pressure reaching 200 MPa. In these experiments [15] the sample was settled in a small plastic pouch. This experimental apparatus was upgraded [16] switching to a differential system with two cells and pentane as the pressurisation fluid.

This paper presents a comparison of these [14, 16] calorimeters, operating with a single cell and with two cells (viz., differential), respectively, which are both high pressure constant mass calorimeters working in isothermal conditions. The comparison concerns the measure of the latent heat if fusion of water at subzero temperature.

Experimental

Apparatus

The single cell and the differential high pressure apparatus are schematically shown in Figs 1 and 2 respectively. The single cell system [15] used a Calvet calorimetric head which was 70 mm in diameter and 170 mm in height. 400 thermocouple junctions were radially installed between the central calorimetric cavity (17 mm diameter) and the external wall of the cell. The high pressure cell was machined in a rod of APX steel (Aubert et Duval, France). The cell was 75 mm long, 17 mm external diameter, 7 mm internal diameter and its effective volume was 1.4 cm^3. The head was installed in an aluminium cylinder (220 mm diameter, 220 mm high) embedded in sand in a 30 cm diameter flask. The temperature was kept constant thanks to a temperature controlled fluid circulating in a copper coil along the outer surface of the flask. Mercury was used as a pressurisation fluid. The differential system used a calorimetric measurement head (Pass 27, SCERES, Orsay, France) which was 170 mm in diameter and 400 mm in height. The calorimetric sensor was composed of 220 thermocouples installed between the two calorimetric cavities whereas two platinum temperature sensors were installed under each of these cavities. An oven installed around the system was used to control the temperature of the calorimetric head. Two high pressure cells were placed in the calorimetric cavities. Electronics (SCERES A/D converter, Orsay, France) and computer systems digitised and recorded the temperatures and the calorimetric signal.

The pressurisation system and tubing were the same for both calorimeter. Cells were connected to a high pressure tube (3.2 mm diameter or 1/8 inch) thanks to Harwood miniature fittings (M2 Serie, 100 MPa, Harwood Engineering, Ma, USA). A high pressure capillary tube (1.6 mm diameter or 1/16 inch) was silver brazed to the 3.2 mm high pressure tubing close to the cells to minimise heat losses between the calorimeter head and the ambient. A T-fitting was used for the differential system to pressurise both cells. Sealing of the cell was obtained with a metallic cone applied against a square hedge in the single cell calorimeter (Chourot, 1997 [14]). A scheme

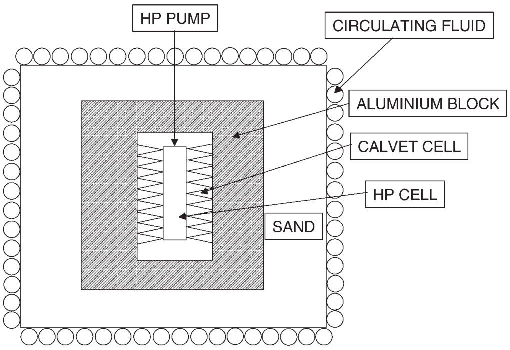

Fig. 1 Scheme of the single cell calorimeter installation. Pressurisation setup was similar to the differential calorimeter

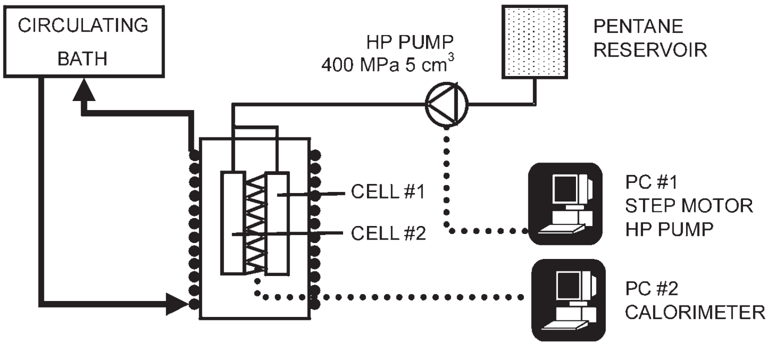

Fig. 2 Scheme of the differential high pressure calorimeter

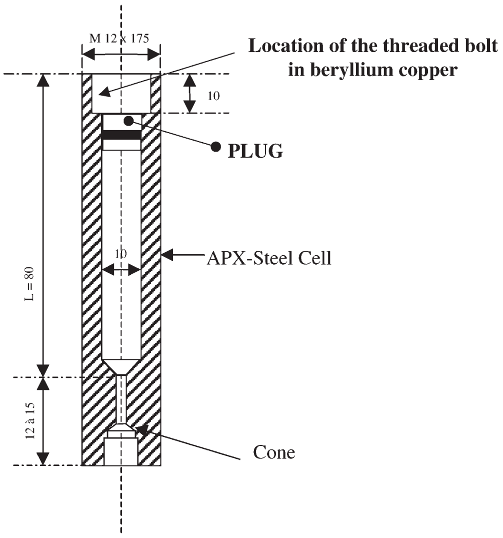

Fig. 3 High pressure cell (differential apparatus). Dimensions are in mm

of the cell used in the differential calorimeter is shown in Fig. 3. The effective volume of the cell was 4.6 cm^3. A plug (Fig. 4) was installed in the cell and a threaded copper-beryllium bolt was finally installed to stop the plug. A nitrile O-ring seal was installed in a slot machined in the plug. Cells and plug were machined in APX steel (Aubert et Duval, France).

A high pressure compressor (400 MPa, 5 cm^3, Nova-Swiss, Effretikon, CH) was driven by a step motor (MIJNO MO63-LE09) and was connected to the pressure inlets. A pressure sensor (200 MPa, Asco Instruments, Chateaufort, France) was used to monitor the pressure. A PID software was developed to drive the motor.

Mercury was chosen as a pressurisation fluid in the single cell calorimeter. Mercury has two major advantages. Firstly, it remains in the liquid state in a wide range of pressure at subzero temperatures. Secondly, the heat dissipated by this fluid during a pressure evolution is very small thanks to a small coefficient of thermal expansion. Pentane (Sigma, St. – Quentin Fallavier, France) was chosen as pressurisation fluid for the differential system because of its stability on the pressure-temperature domain tested and its properties (low viscosity, no phase change).

Calibrations

The pressure sensor was calibrated against a Bourdon reference pressure gauge (Bourdon, France). The calorimeter temperature was calibrated against a 0.1 mm diameter K-type thermocouple (Omega, USA) placed in the sample cell at selected temperature between –20 and +20°C. The calibration of the calorimeters was carried out by Joule effect using a 100 Ω resistance settled in a high pressure cell. A voltage between 1 and 4.2 V was applied to this resistance for period between 30 and 90 min.

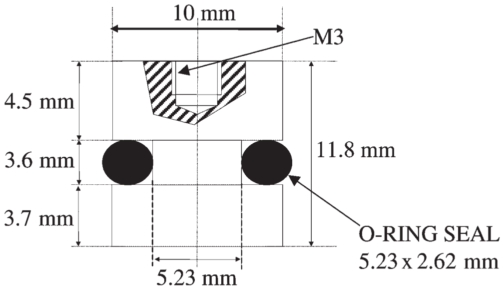

Fig. 4 Scheme of the plug equipped with an O-Ring (5.23 mm int diam.×2.32 tore diam). This plug was installed in the cell shown in Fig 3. A screw was installed in the M3 thread to withdraw the plug from the cell. A beryllium–copper bolt was stopping this plug (not shown)

The power dissipated in the resistance was evaluated with the voltage and the current measured with a voltmeter (programmable voltage source, Keithley) and an ampere meter (digital multimeter, Keithley). The calorimetric peak due to the power step was recorded and its integration allowed to calculate the sensibility coefficient at selected temperatures. The experimental sensibility was evaluated between –15 and 5°C for the single cell system and between –20 and 0°C for the differential system. A linear fit of the experimental data yielded Eq. (1) for the single cell calorimeter and Eq. (2) for the differential calorimeter.

$$\sigma(T)=8.28\cdot 10^{-4}T^2-8.32\cdot 10^{-3}T+16.12\ (\mathrm{W\ V^{-1}}),\ T \text{ in °C} \tag{1}$$

$$\sigma(T)=-3.20\cdot 10^{-3}T+0.613\ (\mathrm{mW}),\ T \text{ in °C} \tag{2}$$

Deconvolution

A deconvolution of the calorimetric signal was developed to reduce the pressure span of the peaks. The pressure span is the pressure difference between the beginning and end of a peak. A detailed procedure is presented in [17]. The sample generates a signal called thermogenesis. This signal is modified by the calorimeter which delivers a signal called calorimetric curve. The calorimeter being regarded as a linear system, this calorimetric curve is the product of convolution between the thermogenesis and the impulse response of the system. The thermogenesis can be calculated by deconvolution of the calorimetric curve. The calorimeter model is considered as a transfer function in Z-function form. A pseudo-random binary sequence (PRBS) $u(t)$ is applied (Joule effect) with a voltage to the calibration resistance inside the cell. The parameters of the calorimeter model are modified in order to minimize the difference between the measured signal, $y(t)$, and the model output, $\hat{Y}(t)$ (Fig. 5). A recurrence equation between $y(t)$ and $Y(t)$ is straightforwardly deduced. This equation allows to calculate the entry of the system, namely, the thermogenesis, from the output, which is the calorimetric curve.

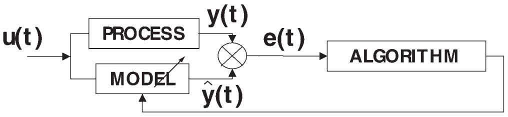

Fig. 5 Algorithm of the deconvolution procedure

Results and discussion

Validation

The high pressure calorimeters were validated by measuring the latent heat of melting of ice into water. The water sample (≈1 g) was vacuum-packaged in a polyethylene bag and placed in the high pressure sample cell. Heat dissipated during isothermal compression d*P* of a substance is given by Eq. (3).

$$dQ=\alpha VTdP \tag{3}$$

where α is the isobaric expansion coefficient and *V* is the volume of the sample. For the single cell system, the heat dissipated by the mercury was negligible in comparison to the latent heat of water. In order to minimise the heat dissipated by pentane in the reference cell for the differential system, the volume of the sample (in the measuring cell) was replaced by a nylon rod (in the reference cell) with a volume equivalent to that of the water sample placed in the measuring cell. Nylon was chosen because of its low compressibility and the absence of phase change in the pressure and temperature domain considered. The calorimeter was then cooled to the temperature of treatment overnight inducing the freezing of the water sample *in situ*. The pressure was then increased at a constant rate (range between 0.2 and 1 MPa min^{-1}) from 0.1 to 200 MPa. When the pressure reached the corresponding phase change temperature (temperature of the calorimeter), the samples started melting. The melting phenomenon associated to the pressure increase makes the sample temperature to decrease. This induced a heat transfer through the heat flux sensors. The peak increased until complete melting of the sample and declined back to the initial base line.

Three calorimetric plots obtained with the single cell system at –10, –7 and –5°C with a 0.24 MPa min^{-1} pressurisation rate are presented in Fig. 6. An experimental plot obtained with the single cell calorimeter is presented in Fig. 7 with a 1 MPa min^{-1} pressurisation rate. A plot obtained in similar conditions with the differential system at –7.3°C is shown in Fig. 8. An important difference between the two plots (Fig. 7 *vs.* 8) is that with the single cell, the phase change peak is spanned over 50 MPa while with the differential system, the peak is spanned over 60 MPa. This difference can be explained by the fact that mercury was used as a pressurisation fluid instead of pentane. The higher thermal conductivity of mercury resulted in an improvement of the heat transfer between the sample and the cell, resulting in a thinner peak (thickness of the wall was 5 mm for both cells). The Calvet cell was also more conductive than the differential calorimeter head. The impact of the pressurisation rate appears clearly by comparing Figs 6 and 7 which were obtained with the single cell calorimeter. The peak span was around 30 and

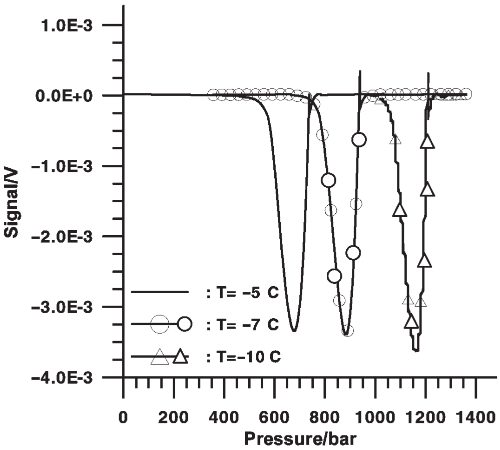

Fig. 6 Experimental plots obtained with the single cell calorimeter. Pure water, $T=-5/-7/-10°C$, sample mass≈0.9 g, pressurisation rate 0.24 MPa min^{-1}

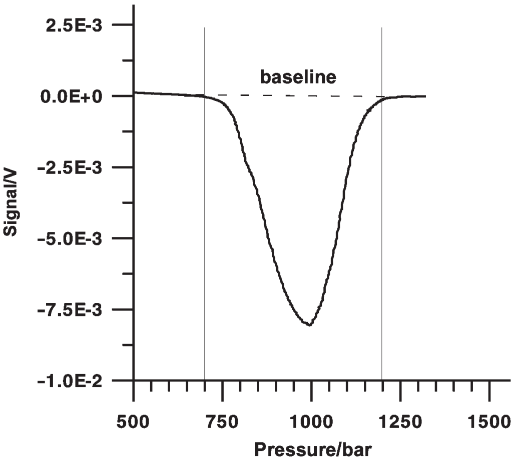

Fig. 7 Experimental plot obtained with the single cell calorimeter. Pure water, $T=-7°C$, sample mass ≈1 g, pressurisation rate 1 MPa min^{-1}

50 MPa for 0.24 and 1 MPa min^{-1} pressurisation rate respectively. This results showed that as for isobaric calorimetry, a higher scanning rate (pressure or temperature) yield a larger span of the peak. This result is due to the large heat capacity of the cells which store heat during phase change (when calorimetric signal is increasing) and has to release the heat after the phase change (decline of the peak). The duration of the decline of the peak, until it reaches the base line, is a characteristic time function of the heat transfer coefficient between the cell and the surrounding (calorimeter). Thus a faster scanning rate will result in a larger pressure span of the peak. Some alternatives to the constant pressurisation rate have been developed such as [13] who used pressure step comprised between 1 and 20 MPa [4] showed results with pressurisation rates between 0.3 and 1.2

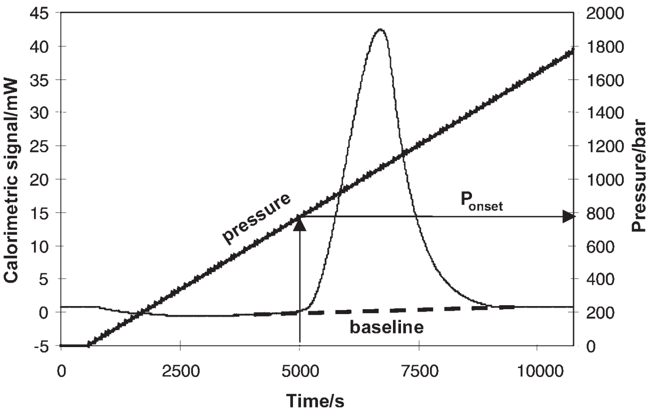

Fig. 8 Experimental plot obtained with the differential calorimeter. Pure water, $T=-7.3$°C, sample mass ≈1 g, pressurisation rate 1 MPa min^{-1}

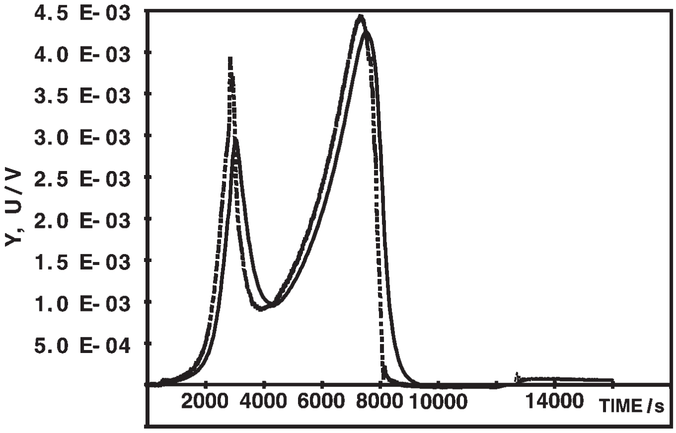

Fig. 9 Melting peak of a $MgSO_4$ solution (9.7% mass/mass) obtained with the single cell calorimeter. Calorimetric curve = — original signal from the calorimeter, thermogenesis = ▮▮▮ deconvoluted signal, $T=-6$°C, sample mass 0.7442 g, pressure scan at 0.5 MPa min^{-1}

MPa min^{-1}. He observed a peak span of 70 MPa at 0.3 MPa min^{-1} for the solid-liquid transition in benzene at 314.2 K. The major limitation in using slower pressurisation rate was the duration of the experiment rather than technical reasons. The slower the pressurisation rate was, the thinner the peak. An onset pressure, which defined the pressure of the beginning of melting, as well as a peak pressure were graphically determined as shown in Fig. 8. The onset was considered when the calorimetric signal showed a detectable departure from the base line. Indeed, this phenomenon was directly linked to the beginning of the melting of the sample. The tangent to the increasing part of the peak can be considered as well as this is usually realised for conventional calorimetry.

The latent heat was evaluated by integrating the calorimetric peak corrected by the sensibility coefficient and after subtraction of the base line. The base line was obtained by linking the base line before and after the phase change peak. This procedure was carried out at four different temperatures (–5, –7, –9.3 and –10°C) and was duplicated at each temperature with the single cell calorimeter. Three different temperatures (–5, –10 and –15°C) were investigated with differential calorimeter with four measurements at each temperature. The comparison between the experimental results and the data proposed by Bridgman [6] are tabulated in Tables 1 and 2 for the single cell calorimeter and the differential calorimeter respectively. These results showed a small deviation (≈1.3 to 3.42%) from the data obtained by Bridgman [6] who used Clapeyron's relation to calculate the latent heat. The single cell calorimeter was able to make accurate measurement with sample between 0.3 and 1 g while a 1 g minimum mass sample was required for the differential system due to a heavy cell. Larger sample can be used but tend to increase the pressure span of the peak whereas smaller masses were still acceptable but tend to increase the noise to signal ratio. These masses were found as a good balance between peak span and noise to signal ratio. This good agreement allowed us to consider this apparatus reliable to evaluate the latent heat of products under pressure.

Table 1 Single cell calorimeter. Latent heat of water (mean of 2 experiments) according to the set temperature and the deviation from the Bridgman data [6] (1912-b). Mass of sample between 0.3 and 1 g

Temperature/°C	Experimental latent heat/J g^{-1}	Bridgman data [6]	Deviation from Bridgman data [6]/%
–5.0	297.0	307.6	–3.4
–7.0	290.5	298.0	–2.5
–9.3	282.5	287.3	–1.7
–10.0	275.0	284.0	–3.2

Table 2 Differential calorimeter. Latent heat of water (mean of 4 experiments) according to the set temperature and the deviation from the Bridgman data [6] (1912-b). Mass of sample ≈1 g

Temperature/°C	Experimental latent heat/J g^{-1}	Standard deviation	Bridgman data [6]	Deviation from Bridgman data [6]/%
–5	297.6	2.6	307.6	–3.2
–10	274.6	2.1	284.0	–3.3
–15	265.3	5.8	261.9	+1.3

The deconvolution was used to reduce the pressure span of the peak. A typical result is presented in Fig. 9. The melting peak was obtained with a magnesium sulfate aqueous solution and showed an eutectic peak (first peak) followed by the melting of the ice in solution mixture. The deconvolution permitted to improve the definition of the peak. Similar application done with pure water permitted to reduce the span of the peak by 30%. These first encouraging applications should be followed by a systematic use of this conventional but efficient technique.

Conclusions

This work evaluates two high pressure calorimeters via determination of the ice melting latent heat in isothermal conditions. The pressurisation circuit allows a constant rate pressure increase. The single cell system gave slightly thinner peaks than the differential system due to the use of mercury instead of pentane as a pressurisation fluid which improves heat transfer. Mercury offers the advantage of a higher heat transfer but requires more care during manipulation. A slower pressurisation rate combined to a minimised mass of sample permits to reduce the span of the peak. Future development will probably aim to improve the response time of the calorimeter by using smaller cells or more conductive cells (i.e. using copper–beryllium alloy). Reducing the size of the cell will be limited by the ratio between the size of the cell and the dimension of the high pressure tubing and fittings which induces a significant heat loss toward the ambience. Harwood fittings which were used in the present case were found to be the smallest high pressure fitting available on the market and are very efficient in miniaturisation of the connection with the cells. Further development which should include a systematic use of the deconvolution technique will permit to reduce the pressure span of the peak.

Nomenclature

P	pressure	MPa
Q	heat	J
T	temperature	°C
V	volume	m^3
α	isothermal compressibility	K^{-1}
σ	sensitivity	WV^{-1} or mW

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