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DYNAMIC CALORIMETRY IN HIGH-PRESSURE, HIGH-TEMPERATURE THERMODYNAMICS OF LIQUIDS *,**

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ABSTRACT

Applications of pressure-controlled scanning calorimetry in thermodynamic investigation of liquids under high pressure and at high temperatures are analyzed. A novel method for the determination of excess thermodynamic functions under pressures up to 400 MPa and at temperatures up to 500 K is described.

It is an honour for the author to have the opportunity to thank Professor Wendlandt for his efforts to facilitate development of dynamic thermal techniques by the acceptance and rapid publication of recent results from different research groups all over the world. Much has already been achieved, but a lot can still be done in this permanent struggle between the accuracy and the speed of measurements and in a proper adjustment of the measuring technique to the nature of the process under investigation. In the present paper, dedicated to Professor W.W. Wendlandt, the author attempts to present applications of pressure-controlled scanning calorimetry, a relatively new dynamic calorimetric technique, in the investigation of thermodynamic properties of liquids.

INTRODUCTION

The pressure variable has been greatly neglected in thermodynamic investigation on liquids, although its importance in the theories of the liquid state has been known for a long time [1]. In recent years there has been a growing interest in high pressure investigation of thermal properties of liquids, mainly by application of flow calorimetric techniques. However, most of these studies use high pressure because of the inherent high vapour pressure

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or because of the risk of decomposition of the substance under investigation. Therefore, one can say that the pressure is used in these studies as a dependent variable. The aim of this paper is to present the thermodynamic possibilities of using pressure as an independent thermodynamic variable. Dynamic calorimetric techniques are very useful in this kind of investigation, in which pressure-controlled scanning calorimetry plays an important role. The basic thermodynamic foundation of the method is the identity which when written in the differential form is as follows

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right]b=\left(\frac{\partial S}{\partial p}\right)_T\cdot T\cdot b=-\left(\frac{\partial V}{\partial T}\right)_p\cdot T\cdot b \tag{1}$$

where b is the rate of a continuous pressure scan, and when written in the integral form is

$$\Delta_{p_1}^{p_2}Q=\int_{p_1}^{p_2}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right]\mathrm{d}p=T\int_{p_1}^{p_2}\left(\frac{\partial S}{\partial p}\right)_T\mathrm{d}p=-T\int_{p_1}^{p_2}\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p \tag{2}$$

The technical and experimental details of the present method have been described by Ter Minassian and coworkers for step-wise pressure scanning (piezothermal method) [2,3] and by the present author for continuous pressure scanning [4–6] and will not be presented here. The use of pressure as an independent thermodynamic variable usually requires large pressure intervals in order to be able to measure the pressure effect with sufficient precision. The use of high pressure naturally results in the use of massive experimental vessels and the necessity of connecting them to a pressure generator. This usually eliminates or greatly limits applications of other known thermodynamic techniques such as adiabatic calorimetry. Dynamic calorimetric techniques are thus obviously important in such investigations. Recent results are presented below in the discussions of particular thermodynamic functions, with a special emphasis on the determination of pressure influence on the excess thermodynamic functions at high temperatures, where there is an almost complete lack of data in the up-to-date literature.

HEAT CAPACITY

Heat capacity is most directly related to the structure of the liquid state, although not many studies have been devoted to this subject [7]. The first information that the effect of pressure on the heat capacity of liquids can have unusual and bewildering behaviour came from volumetric measurements by Bridgman [1,8]. Although it is probable that not all of his observations are true, it has been confirmed that the dependence of pressure on the heat capacity of liquids has an interesting character. As an example, the influence of pressure on the heat capacity of n-hexane at 353.15 K is

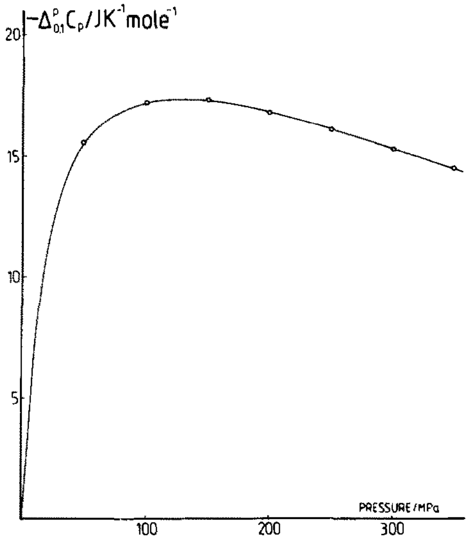

Fig. 1. The influence of pressure on the heat capacity of n-hexane at 353.15 K.

presented in Fig. 1. This behaviour was determined on the basis of the following relation [9,10]

$$\Delta^{p}_{0.1\mathrm{MPa}}C_{\mathrm{p}} = -T\int_{p_0}^{p} V(303.15,\ p)\exp\left[\int_{303.15}^{T}\alpha(T,\ p)\,\mathrm{d}T\right]\left(\alpha^2+\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\mathrm{d}p \tag{3}$$

using data from the calorimetric measurements of thermal expansivity, $\alpha(T,\ p)$, of Pruzan [11] and the volumetric data, $V(303.15,\ p)$, of Eduljee et al. [12]. From Fig. 1 one can see that the heat capacity of n-hexane demonstrates a minimum in its dependence on pressure. The heat capacity of other pure organic liquids, such as n-butane investigated in a pressure-controlled calorimeter over the temperature interval 250–400 K [13], 3-methylpentane [14], n-pentane and n-heptane [15] investigated in a diathermic calorimeter at 298–300 K, and n-octane investigated with the volumetric technique at 318 K [16], demonstrate a similar high-pressure behaviour. The heat capacity of a coal-derived liquid (a complicated organic mixture) under pressure up to 350 MPa and at temperatures up to 447 K determined on the basis of the calorimetric and volumetric data of the present author has been recently reported and at high temperatures a similar pressure behaviour has been observed [10]. It was also reported, on the basis of both pressure-controlled [9] and diathermic [17] calorimetric measurements, that the heat capacity of water demonstrates a similar behaviour, although the minimum appears at much higher pressures than is observed for organic liquids. The elucidation of this behaviour of the heat capacity on the basis of existing theories of liquids is difficult, but the observation of the behaviour of thermal expansion as a function of both pressure and temperature can be helpful, as can be seen from the next section.

THERMAL EXPANSION

The pressure dependence of heat capacity is described by the thermodynamic formula

$$\left(\frac{\partial C_{\mathrm{p}}}{\partial p}\right)_p = -VT\left(\alpha^2 + \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) \tag{4}$$

It is known from numerous pressure-controlled scanning calorimetric measurements [e.g. 11,13,18] that isotherms of thermal expansion, α, as a function of pressure at different temperatures demonstrate a crossing point, at least for simple liquids. At pressures below the crossing point the temperature derivative of thermal expansion is positive and above the crossing point at the high pressures it is negative. This observation in connection with eqn. (4) gives a phenomenological thermodynamic explanation of the pressure dependence of the heat capacity of liquids [9,14]. An attempt has also been made to give an explanation of this behaviour on the molecular level [16]. The basic idea of this concept is an assumption that a liquid under pressure is packed in such a manner that it can be represented by a system of oscillators, as is assumed in the so-called oscillator theory of liquids. If such is the case then the main contribution to the thermal expansion comes from the anharmonicity of oscillations. The anharmonicity of oscillation is caused by the lack of symmetry in the intermolecular potential with regard to the mean separation distance. Because of lack of symmetry, an increase in the energy of oscillation caused by a rise in the temperature of the system leads to an increase in the mean separation distance; the amount of this increase depends on the actual shape of the intermolecular potential. Because the thermal expansion is directly related to the change in intermolecular separation, it can be said that the change of the temperature derivative of thermal expansion with pressure is caused by a change in the shape of the intermolecular potential and it can be concluded that an application of pressure to a liquid markedly changes its intermolecular potential. More detailed discussion of this model explaining the pressure dependence of both the heat capacity and the thermal expansion can be found in ref. 19.

Determination of both $C_{\mathrm{p}}(T, p)$ and $\alpha(T, p)$ enables one to find other thermodynamic functions, such as $\Delta H(T, p)$, $\Delta S(T, p)$ and $\beta(T, p)$, of the liquid under investigation at given pressure and temperature intervals. An example of such a procedure has been given for a coal-derived liquid [10].

SOLID-LIQUID TRANSITIONS

Pressure-controlled scanning calorimetry is a suitable technique for investigating phase transitions, although most of the known applications of scanning calorimetry in this field, including those at high pressures [20], have used the temperature-controlled technique. The use of pressure as an inducing parameter has an important difference in comparison to the use of temperature as such a parameter. In a temperature-controlled experiment the rate of power evolution in the course of fusion is determined by the rate of temperature changes and by the heat exchange coefficient [21]. In a pressure-controlled experiment the rate of pressure scan and the heat exchange coefficient as well as the coefficient $\mathrm{d}p/\mathrm{d}T$ of the transition under investigation play an important role in the determination of the power evolution, that is, of the observed rate of phase transition [5]. The advantage of this property is that from one thermogram of transition, recorded with a pressure-controlled instrument, one can determine, besides the enthalpy of fusion, such important thermodynamic parameters as the temperature of fusion, T_f, the pressure of fusion, p_f and $\mathrm{d}p/\mathrm{d}T$ if the calorimeter is properly calibrated. Unfortunately it also has a disadvantage: the measurements can be, for some substances, very slow, time consuming and can take place over large pressure intervals. However, it is not quite clear whether these remarks can be connected to the inherent features of fusion of organic substances; particularly the very large pressure interval of transition, recorded with the step-wise pressure programming in constant (continuous) volume calorimetric vessels must be explained [22]. Further studies are needed to elucidate this phenomenon more precisely and to decide whether it is a physical property or an interposition of experimental artifacts.

EXCESS THERMODYNAMIC FUNCTIONS

The description of thermodynamic properties of liquids is often made with the use of excess functions. The pressure derivatives of these functions can be written as follows [23]

$$\left(\frac{\partial H^\mathrm{E}}{\partial p}\right)_T = V^\mathrm{E} - T\left(\frac{\partial V^\mathrm{E}}{\partial T}\right)_p \tag{5}$$

$$\left(\frac{\partial G^\mathrm{E}}{\partial p}\right)_T = V^\mathrm{E} \tag{6}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V^\mathrm{E}}{\partial T}\right)_p \tag{7}$$

As can be seen, the molar excess volume, V^E, is the most important parameter in this description. However, the precise measurements of volume at high pressure and at high temperatures are difficult, and up-to-now no such data obtained at high temperature have been reported. The calorimetric flow technique is very useful in direct measurements of excess enthalpy, but its use is limited to about 60 MPa. Pressure-controlled scanning calorimetry has not been used previously in the determination of excess functions. However, its application is possible through the determination of thermal expansion. An example of such a procedure is presented here for a binary mixture.

From the thermodynamic definition of thermal expansion one can write

$$V_n(T, p) = V_n(T_0, p) \exp\left[\int_{T_0}^{T} \alpha_n(T, p)\,\mathrm{d}T\right] \tag{8}$$

and

$$\left[\frac{\partial V_n(T, p)}{\partial T}\right]_p = \alpha_n(T, p) V_n(T_0, p)\left[\int_{T_0}^{T} \alpha_n(T, p)\,\mathrm{d}T\right], \tag{9}$$

where $n = \mathrm{s}$, 1 or 2 and describes the binary solution (s), the component (1) and the component (2). In order to simplify the writing of formulas the following substitution is introduced

$$A_n(T, p) = \exp\left[\int_{T_0}^{T} \alpha_n(T, p)\,\mathrm{d}T\right] \tag{10}$$

The molar excess volume of a binary mixture is defined as follows

$$V^{\mathrm{E}}(T, p) = V_{\mathrm{s}}(T, p) - x_1 V_1(T, p) - (1 - x_1) V_2(T, p), \tag{11}$$

where x_1 is the molar fraction of component 1. From eqns. (5–11) the thermodynamic formulas for the determination of the pressure influences on excess functions can be written as follows

$$\begin{aligned}\Delta_{p_0}^{p} G_T^{\mathrm{E}} = {} & \int_{p_0}^{p} V_{\mathrm{s}}(T_0, p) A_{\mathrm{s}}(T, p)\,\mathrm{d}p - x_1 \int_{p_0}^{p} V_1(T_0, p) A_1(T, p)\,\mathrm{d}p \\ & - (1 - x_1) \int_{p_0}^{p} V_2(T_0, p) A_2(T, p)\,\mathrm{d}p,\end{aligned} \tag{12}$$

$$\begin{aligned}\Delta_{p_0}^{p} H_T^{\mathrm{E}} = {} & \int_{p_0}^{p} V_{\mathrm{s}}(T_0, p)[1 - \alpha_{\mathrm{s}}(T, p) T] A_{\mathrm{s}}(T, p)\,\mathrm{d}p \\ & - x_1 \int_{p_0}^{p} V_1(T_0, p)[1 - \alpha_1(T, p) T] A_1(T, p)\,\mathrm{d}p \\ & - (1 - x_1) \int_{p_0}^{p} V_2(T_0, p)[1 - \alpha_2(T, p) T] A_2(T, p)\,\mathrm{d}p,\end{aligned} \tag{13}$$

$$\begin{aligned}\Delta_{p_0}^{p} S_T^{\mathrm{E}} = {} & x_1 \int_{p_0}^{p} V_1(T_0, p) \alpha_1(T, p) A_1(T, p)\,\mathrm{d}p \\ & + (1 - x_1) \int_{p_0}^{p} V_2(T_0, p) \alpha_2(T, p) A_2(T, p)\,\mathrm{d}p \\ & - \int_{p_0}^{p} V_{\mathrm{s}}(T_0, p) \alpha_{\mathrm{s}}(T, p) A_{\mathrm{s}}(T, p)\,\mathrm{d}p\end{aligned} \tag{14}$$

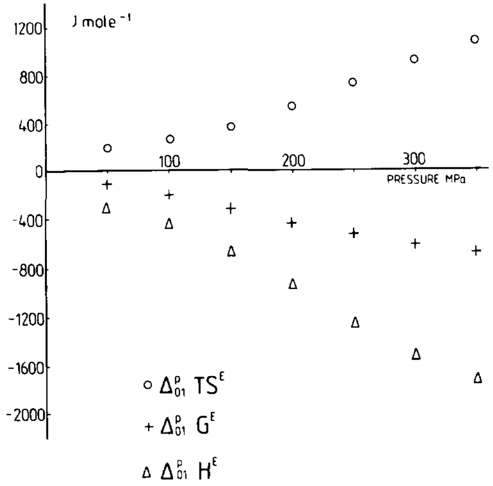

Fig. 2. The influence of pressure on the thermodynamic excess functions in 0.5 *m*-cresol–0.5 quinoline mixture at 503.15 K.

One can see that a determination of the influence of pressure on the main thermodynamic excess functions of a binary solution requires three sets of data (for the solution and the two components) for thermal expansion as a function of pressure and temperature and three sets of data on respective volumetric isotherms at the reference temperature, which can be the lowest temperature at which the calorimetric measurements have been performed, and at the pressure interval under investigation. The measurements require relatively small amounts of substances and can be automated. An example of results obtained with this procedure is presented in Fig. 2, where the influence of pressure on the excess functions of 0.5 *m*-cresol + 0.5 quinoline mixture at 503 K is given. The detailed thermodynamic data on this system and a description of a newly constructed pressure-controlled scanning calorimeter will be published elsewhere.

Unfortunately, we could not compare and verify the present data with the literature data because of a complete lack of the latter. However, one can see that the method does not require any differentiation, which is the main source of errors when using volumetric data, and the measurements of thermal expansion can be always checked with other systems, such as n-hexane, which can become a standard liquid in this type of investigation [11].

CONCLUSIONS

The application of pressure-controlled scanning calorimetry in the investigation of thermodynamic properties of liquids has two principal advantages:

(1) it permits the determination of the influence of pressure on the thermodynamic functions at very large pressure intervals, (2) it can be used at high temperature under high pressure where other known techniques fail. The precision of the primary experimental data is of the order 1–3% over the whole pressure and temperature intervals [2]. The precision in the calculated final thermodynamic values is not degraded as much as it is in the case of volumetric measurements, where the first and second order derivatives of experimental data are needed.

Although pressure-controlled scanning calorimetry is a relatively new technique, it has already provided interesting experimental data, such as a minimum in the heat capacity dependence on pressure, a crossing point on the plot of thermal expansion vs. pressure at different temperatures, and the thermal expansion behaviour in the vicinity of the solid–liquid transition induced by pressure. These experimental facts together with the data on the influence of pressure on the excess functions obtained with the method presented in this paper can be of importance in elucidating the nature of the liquid state over large intervals of pressure and temperature.

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