Transitiometry for measurements of physical properties under high pressure

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For applications like radical polymerisation of LDPE, physical properties are of interest reflecting high pressure as a process condition. Applying this data, the modelling of this process can be optimized. Available literature end at medium pressure and mostly interpolates up to higher pressure. To measure directly under high pressure, the number of suitable methods and devices are considerably decreased due to the required massive construction and stable materials. Transitiometer from BGR TECH enables calorimetry under high pressure. A transitiometer controls the three most important thermodynamic variables of temperature, pressure and volume beside the calorimetric signal.[1] Isobaric mode up to 3000 bar is realized using a step motor and allow the investigation of pressure dependence. In the different modes, the first physical property is kept constant, the second following an applied function and the third is affected by this (Fig.1).

Figure 1 Modes of transitiometer with derivable physical properties.

input		thermal output	mechanical output
$dT = 0$, $p = f(t)$	⇨ pVT-schedule ⇨	$\left(\frac{\partial S}{\partial p}\right)_T \rightarrow \alpha_p$	$\left(\frac{\partial V}{\partial p}\right)_T \rightarrow \kappa_T$
$dT = 0$, $V = f(t)$	⇨ pVT-schedule ⇨	$\left(\frac{\partial S}{\partial V}\right)_T \rightarrow \beta_V$	$\left(\frac{\partial V}{\partial p}\right)_T \rightarrow \kappa_T$
$dp = 0$, $T = f(t)$	⇨ pVT-schedule ⇨	$\left(\frac{\partial H}{\partial T}\right)_p \rightarrow c_p$	$\left(\frac{\partial V}{\partial T}\right)_p \rightarrow \alpha_p$
$dV = 0$, $T = f(t)$	⇨ pVT-schedule ⇨	$\left(\frac{\partial U}{\partial T}\right)_V \rightarrow c_V$	$\left(\frac{\partial p}{\partial T}\right)_V \rightarrow \beta_V$

A high number of thermocouples is necessary for a transitiometer for sufficient thermal sensitivity due to the pressure-induced massive mounting. This high sensitivity is assured using 672 thermocouples for the Standard Unit and 1344 for Advanced Unit in a Tian-Calvet-design and a sample volume of 1 mL.

Due to their pressurizing system, the Standard Unit suits liquid and meltable samples and the Advanced Unit suits gases. For these samples, pressure-dependent physical properties like density, compressibility, thermal expansion coefficient and heat capacity can be investigated. Furthermore, the kinetic of significantly exothermal or endothermal reactions like peroxide decomposition can be monitored. The pressure and temperature dependent properties can be expressed by empirical equations of PC-SAFT parameters, which are fitted to the measured data. This information could be used for modelling purposes.

To decreases possible errors or deviations, modes of measurements are compared, temperature and enthalpy is calibrated, a correction of device-dependent is done and the evaluation is unified.

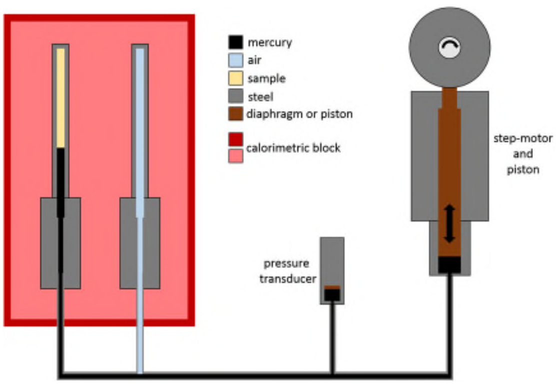

Figure2 Schematic cross section of Standard Unit Transitiometer.

[1] S.L. Randzio, Chem. Soc. Rev. 25 (1996) 383.