

# High pressure thermal expansion of gases: measurements and calibration

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## Abstract

A set-up based on transitiometric principles has been designed for direct measurements of high pressure cubic expansion coefficient of gases. A new method of calibration was presented for pressure-controlled calorimeters working with open mass calorimetric vessels. The new method is based on heat capacity standards and thus is a complementary to the previous methods based on thermal expansion standards. The calibrations performed with the new method using a number of heat capacity standards demonstrated that the calibration constant of correctly designed calorimetric vessels does not depend on pressure. The results of test measurements with nitrogen performed accordingly to the thermodynamic foundations of the method are in satisfactory agreement with the literature data.

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## 1. Introduction

Cubic expansion coefficient ( $\alpha$ ) is the second mix derivative of the Gibbs potential against pressure and temperature. Its knowledge is of great importance for both scientific and industrial purposes. For example, availability of  $\alpha$  over large ranges of pressure and temperature is an extremely useful means in adjustment of parameters in new equations of state [1]. Moreover, thermodynamic relationships show that the cubic expansion coefficient represents an alternative route to the estimation of the inversion Joule–Thomson  $\mu_{J-T}$  curve whose determination is of great importance in oil and gas industries. An important progress has been made with respect to the direct determination of  $\alpha$  for liquids at high pressures and temperatures [2,3]. However, for gases the most of the existing data were derived from  $pVT$  measurements or from empirical equations of state based on them, especially at high pressure conditions. The aim of the present study is to elab-

orate an experimental set-up for direct measurements of the cubic expansion coefficient of gases performed over wide pressure and temperature ranges. The new instrument was designed on the basis of transitiometric principles previously described [4], but its structure and calibration are original and are adapted to the specific properties of gases, such as an extremely high compressibility.

## 2. Experimental set-up

A general view of the experimental set-up is presented schematically in Fig. 1. Calorimetric vessels and a Setaram C80 calorimeter 1 were previously adapted to measure the isobaric heat capacity  $C_p$  of liquids and gases at pressures up to 100 MPa with the temperature-scanning mode [5]. In order to incorporate the pressure-scanning variable a Calpresdat automated high pressure pump (250 cm<sup>3</sup> cylinder) 2 was implemented. The pressure is measured with Viatran 245 transducers 3 (precision  $\leq 0.1\%$  FSO). Volume variations are recorded by counting the stepping motor controlling impulses

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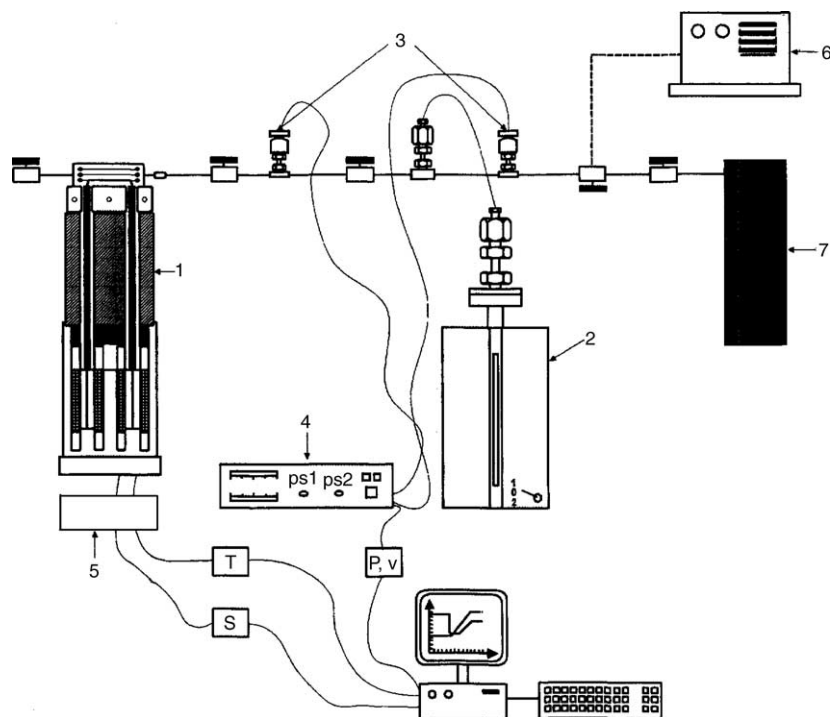


Fig. 1. Schematic diagram of the experimental set-up: (1) C80 calorimeter, (2) Calpresdat automated high pressure pump, (3) Viatran 245 pressure transducers, (4) pump controller, (5) calorimeter controller, (5) vacuum pump, (6) gas tank.

(1 step =  $1.55 \times 10^{-3} \text{ cm}^3$ ). In order to enable a simultaneous control of independent thermodynamic variables, the controllers of both the pump 4 and of the calorimeter 5 have been coupled and the whole set of thermodynamic variables ( $p, V, T$ ) is now controlled with a software written in the LabView graphical programming language [6]. The three state

variables or their variations as well as the calorimetric signal can be simultaneously observed by the experimenter as shown in Fig. 2. The specificity of this apparatus remains especially in the very fine control of pressure variations and in the large volume of the pump cylinder ( $250 \text{ cm}^3$ ), what is extremely important in studies of compressible fluids such as



Fig. 2. A window with a typical general view of the LabView software output (pressure decrease under isothermal conditions).

gases up to 100 MPa. The temperature range from 303.15 to 523.15 K is imposed by the C80 properties.

### 3. Recall of thermodynamic basis

The thermodynamic basis for direct determination of  $\alpha$  is the following Maxwell relation:

$$\left(\frac{\partial S}{\partial p}\right)_T = \alpha V_m \quad \text{and thus} \quad \delta Q = -\alpha V_m T dp \quad (1)$$

where  $\delta Q$  is the quantity of heat liberated or absorbed as a consequence of a pressure variation  $dp$  under isothermal conditions. Eq. (1) is valid for 1 mol of a substance. In a mass-open type calorimetric vessel with an active internal volume  $V_E$  (volume covered by the heat flux detector) the number of moles of a fluid substance under investigation contained in the vessel is  $V_E/V_m$ . Thus, for such a calorimetric vessel Eq. (1) takes the following form:

$$\delta Q = -\alpha V_E T dp \quad (2)$$

This thermodynamic relation is applied to both the calorimetric vessel itself and the gas contained therein. The action of pressure on the vessel has an effect opposite to that on the gas contained inside [2]. The contribution from the calorimetric vessel itself is obtained from the increase of the volume of the wall of the cylinder  $V_{SS}$  when an increase of pressure is applied

$$dV_{SS} = V_E \kappa_{T,SS} dp \quad (3)$$

where  $\kappa_{T,SS}$  is the isothermal coefficient of compressibility of the material from which the vessel was made. When introducing Eq. (3) into the Maxwell relation  $(\partial S/\partial V)_T = (\partial p/\partial T)_V = \alpha_p/\kappa_T$  Eq. (4) is obtained

$$\delta Q_{SS} = V_E \alpha_{SS} T dp \quad (4)$$

The calorimetric output signal is thus a sum of two opposite effects: one from the gas and one from the vessel:

$$\delta Q_{\text{tot}} = \delta Q_{SS} + \delta Q = V_E \alpha_{SS} T dp - V_E \alpha T dp \quad (5)$$

In case of a step-wise technique [2], where a pressure step  $\Delta p$  is applied, the respective quantity of heat  $\Delta Q$  (J) is obtained from the integral  $I$  (V s) of the calorimetric response  $\Delta Q = kxI$  where  $k$  (W/V) is the calibration constant of the

calorimetric detector. Taking this into consideration Eq. (5) can be rewritten in the following final form:

$$\alpha_m = -\frac{k}{V_E} \frac{I}{T \Delta p} + \alpha_{SS} \quad (6)$$

where index  $m$  is for mean values of the respective expansion coefficients over the pressure step applied. One can see from Eq. (6) that the fundamental problem of this direct technique of measurements of the cubic expansion coefficient is the determination of the two calibration constants  $k$  and  $V_E$ . At low pressures the ratio  $k/V_E$  can be taken as one calibration constant and determined in calibration experiments performed at various temperatures with the use of a calibrating gas, for example nitrogen, for which the cubic expansion coefficient at low pressures is rather exactly known. In case of liquids a standard substance can be taken, for example *n*-hexane [7], in order to check the pressure dependence of the calibration constant determined with expansion of a low pressure gas or make high pressure calibration. However, in case of gases such a verification or calibration in open mass vessels could be doubtful, because of possible differences in heat transfer in dense liquids and gases and there is no credible gaseous substance which could be used as a standard for cubic expansion coefficient at high pressures. For this reason in the present study an alternative method of calibration was elaborated based on the heat capacity measurements performed in the same experimental vessel at various pressures. The use of heat capacity as a calibration standard can also help to avoid systematic errors which are possible to appear when using thermal expansion standards.

### 4. Calibration constant $k/V_E$ from $C_p$ measurements

Heat capacity measurements can be performed with the same open-mass calorimetric vessels on the basis of the following relation [5]:

$$C_p = \frac{P_{\text{diff}}(x) - P_{\text{diff}}(bl)}{\rho V_E (dT/dt)} \quad (7)$$

where  $P_{\text{diff}}(x)$  is a differential calorimetric power signal (W) obtained with the calorimetric measuring vessel filled with the fluid under investigation and the reference vessel remaining empty,  $P_{\text{diff}}(bl)$  (W) is a similar signal, but obtained with

Table 1  
Results of calibrations, for details see the text

T (K)	Calibration constant $k/V_E$ (MPa V <sup>-1</sup> s <sup>-1</sup> )							
	From N <sub>2</sub> expansion		From $C_p$ at various pressures with various substances					
		0.1 MPa (C10)	0.1 MPa (C12)	0.1 MPa (C17)	10 MPa (C10)	10 MPa (C6)	40 MPa (C6)	100 MPa (C6)
302.9	4.02 ± 0.04	4.04 ± 0.03	4.03 ± 0.03	4.04 ± 0.03	4.02 ± 0.09	4.05 ± 0.05	4.07 ± 0.05	4.04 ± 0.05
322.9	4.09 ± 0.04	4.04 ± 0.03	4.07 ± 0.03	4.07 ± 0.03	4.06 ± 0.09	4.06 ± 0.05	4.07 ± 0.05	4.06 ± 0.05
352.6	4.17 ± 0.03	4.12 ± 0.03	4.12 ± 0.03	4.12 ± 0.03	4.12 ± 0.09	4.12 ± 0.05	4.13 ± 0.05	4.13 ± 0.05
372.5	4.24 ± 0.04	4.19 ± 0.03	4.18 ± 0.03	4.18 ± 0.03	4.18 ± 0.09	4.18 ± 0.05	4.20 ± 0.05	4.20 ± 0.05
422.2	4.47 ± 0.04			4.43 ± 0.03	4.42 ± 0.10	4.45 ± 0.05	4.47 ± 0.05	4.44 ± 0.05

both reference and measuring vessels remaining empty,  $\rho$  ( $\text{g}/\text{cm}^3$ ) is the density of the fluid under investigation. The differential calorimetric power signal is proportional to the differential calorimetric detector thermopile signal  $E$  (V) via the static calibration constant  $k$  (W/V), as mentioned above. Thus, Eq. (7) can be rewritten in the following form:

$$\frac{k}{V_E} = \frac{C_p \rho (dT/dt)}{E(x) - E(bl)} \quad (8)$$

Thus, taking a fluid for which the heat capacity and the density are precisely known as a function of temperature at several pressures, calibration experiments can be performed and the calibration ratio  $k/V_E$  can be determined.

## 5. Results

The determination of calibration constant  $k/V_E$  by the expansion method was performed at low pressures up to 15 MPa

Table 2  
Results of measurements of the high pressure cubic expansion coefficient,  $\alpha$ , of nitrogen

$P$ (MPa)	$\Delta P$ (MPa)	$\alpha_{SS}$ ( $\text{K}^{-1}$ )	$\Delta\alpha_{SS}$ ( $\text{K}^{-1}$ )	$k/V_E$ ( $\text{MPa V}^{-1} \text{ s}^{-1}$ )	$\Delta(k/V_E)$ ( $\text{MPa V}^{-1} \text{ s}^{-1}$ )	$I$ ( $\mu\text{V s}$ )	$\Delta I$ ( $\mu\text{V s}$ )	$\alpha$ ( $\text{K}^{-1}$ )	$\Delta\alpha$ ( $\text{K}^{-1}$ )	Series
$T = 302.9 \text{ K}$										
15.0	2.0	5.1E-05	5E-06	4.03	3E-02	5.8E+05	1E+04	4.0E-03	1E-04	1
30.0	2.0	5.1E-05	5E-06	4.03	3E-02	5.4E+05	1E+04	3.6E-03	1E-04	1
39.9	1.9	5.1E-05	5E-06	4.03	3E-02	4.61E+05	9E+03	3.22E-03	9E-05	
60.0	2.0	5.1E-05	5E-06	4.03	3E-02	3.87E+05	8E+03	2.62E-03	7E-05	
70.0	2.0	5.1E-05	5E-06	4.03	3E-02	3.57E+05	7E+03	2.43E-3	7E-05	
80.0	2.0	5.1E-05	5E-06	4.03	3E-02	3.21E+05	6E+03	2.24E-03	6E-05	
89.9	1.9	5.1E-05	5E-06	4.03	3E-02	2.95E+05	6E+03	2.09E-03	6E-05	
$T = 322.9 \text{ K}$										
13.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.6E+05	1E+04	3.6E-03	1E-04	1
13.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.7E + 05	1E+04	3.6E-03	1E-04	2
14.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.6E+05	1E+04	3.6E-03	1E-04	1
14.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.7E+05	1E+04	3.6E-03	1E-04	2
15.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.6E+05	1E+04	3.6E-03	1E-04	1
15.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.7E+05	1E+04	3.6E-03	1E-04	2
16.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.6E+05	1E+04	3.6E-03	1E-04	1
16.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.6E+05	1E+04	3.6E-03	1E-04	2
18.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.6E+05	1E+04	3.6E-03	1E-04	1
20.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.5E+05	1E+04	3.6E-03	1E-04	1
30.0	2.0	5.1E-05	5E-06	4.06	3E-02	5.2E+05	1E+04	3.33E-03	9E-05	1
40.0	2.0	5.1E-05	5E-06	4.06	3E-02	4.72E+05	9E+03	3.03E-03	9E-05	1
60.0	2.0	5.1E-05	5E-06	4.06	3E-02	3.87E+05	8E+03	2.50E-03	7E-05	1
60.0	2.0	5.1E-05	5E-06	4.06	3E-02	3.87E+05	8E+03	2.50E-03	7E-05	2
60.0	2.0	5.1E-05	5E-06	4.06	3E-02	3.91E+05	8E+03	2.51E-03	7E-05	3
80.0	2.0	5.1E-05	5E-06	4.06	3E-02	3.32E+05	7E+03	2.12E-03	6E-05	1
$T = 352.6 \text{ K}$										
14.0	2.0	5.1E-05	5E-06	4.12	3E-02	5.2E+05	1E+04	3.09E-03	9E-05	1
30.0	2.0	5.1E-05	5E-06	4.12	3E-02	5.0E+05	1E+04	2.97E-03	8E-05	1
30	2.0	5.1E-05	5E-06	4.12	3E-02	5.0E+05	1E+04	2.99E-03	8E-05	2
40.0	2.0	5.1E-05	5E-06	4.12	3E-02	4.64E+05	9E+03	2.6E-03	8E-05	1
50.0	2.0	5.1E-05	5E-06	4.12	3E-02	4.18E+05	8E+03	2.52E-03	7E-05	1
60.0	1.9	5.1E-05	5E-06	4.12	3E-02	3.75E+05	8E+03	2.32E-03	7E-05	1
70.0	2.0	5.1E-05	5E-06	4.12	3E-02	3.61E+05	7E+03	2.169E-03	6E-05	1
80.0	2.0	5.1E-05	5E-06	4.12	3E-02	3.33E+05	1E+03	2.00E-03	6E-05	1
90.0	2.0	5.1E-05	5E-06	4.12	3E-02	3.10E+05	6E+03	1.86E-03	5E-05	1
$T = 422.2 \text{ K}$										
18.0	2.0	5.1E-05	5E-06	4.42	3E-02	4.55E+05	9E+03	2.44E-03	7E-05	1
22.0	2.0	5.1E-05	5E-06	4.42	3E-02	4.66E+05	9E+03	2.49E-03	7E-05	1
24.0	2.0	5.1E-05	5E-06	4.42	3E-02	4.60E+05	9E+03	2.48E-03	7E-05	1
26.0	2.0	5.1E-05	5E-06	4.42	3E-02	4.53E+05	9E+03	2.38E-03	7E-05	1
28.0	1.9	5.1E-05	5E-06	4.42	3E-02	4.26E+05	9E+03	2.36E-03	7E-05	1
30.0	2.0	5.1E-05	5E-06	4.42	3E-02	4.49E+05	9E+03	2.36E-03	7E-05	1
40.0	2.0	5.1E-05	5E-06	4.42	3E-02	4.21E+05	8E+03	2.25E-03	5E-05	1
50.0	2.0	5.1E-05	5E-06	4.42	3E-02	3.84E+05	8E+03	2.06E-03	5E-05	1
60.0	2.0	5.1E-05	5E-06	4.42	3E-02	3.60E+05	7E+03	1.94E-03	4E-05	1
70.0	2.0	5.1E-05	5E-06	4.42	3E-02	3.42E+05	7E+03	1.84E-03	5E-05	1
80.0	2.0	5.1E-05	5E-06	4.42	3E-02	3.28E+05	7E+03	1.77E-03	5E-05	1
90.0	2.0	5.1E-05	5E-06	4.42	3E-02	3.05E+05	6E+03	6.65E-03	5E-05	1

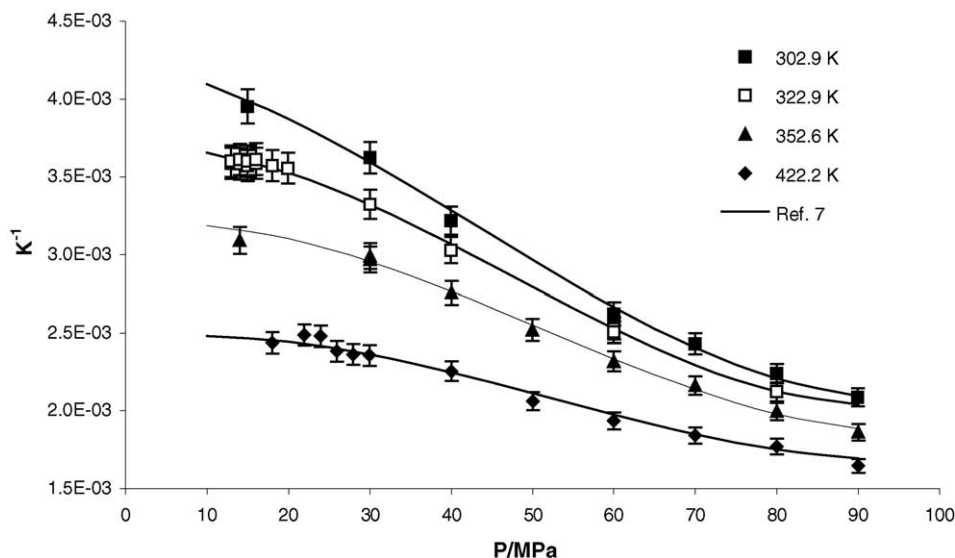


Fig. 3. High pressure cubic expansion coefficient,  $\alpha$ , of nitrogen as a function of pressure.

with the step-wise technique [2] using nitrogen as a calibrating gas [8]. Nitrogen was 99.999% purity, obtained from Messer. The pressure steps of 2 MPa have been performed at a controlled rate of  $0.016 \text{ MPa s}^{-1}$ , which was sufficient to ensure equilibrated heat exchange between the gas, calorimetric vessel and the calorimetric detector under quasi-isothermal conditions required by the Maxwell relation (1) [9]. The results of calibration by the gas expansion method are presented in Table 1, columns 1 and 2. The determination of calibration constant  $k/V_E$  by the isobaric heat capacity method was performed at various pressures with four calibrating substances: *n*-hexane (C6) [7], *n*-decane (C10) [10,11], *n*-dodecane (C12) [11] and *n*-heptadecane (C17) [11]. The temperatures scans were performed at a rate of  $0.016 \text{ K/min}$  ( $2.5 \text{ mK/s}$ ). The results obtained are given in Table 1, columns 3–9. One can see that the calibration constant  $k/V_E$  at respective temperatures does not depend on pressure and within the experimental error is equal to the calibration constant obtained with the gas expansion method. The lack of pressure dependence on the calibration constant of properly constructed calorimetric vessels was previously observed by the liquid step-wise expansion method at high pressures ([2], Table 2). The only dependence of the calibration constant is that on temperature, caused mainly by the change of heat exchange between the calorimetric vessels, calorimetric detector and the environment. Thus, all the data from Table 1 have been fitted to obtain the following equation for the calibration constant as a function of temperature:

$$\frac{k}{V_E}(T/\text{K}) = 5.617 - 1.133 \times 10^{-2}T/\text{K} + 2.0118 \times 10^{-5}(T/\text{K})^2 \quad (9)$$

With that calibration constant test measurements have been performed of thermal expansion coefficient for nitrogen at

pressures up to 100 MPa at selected temperatures (302.9, 322.9, 352.6 and 422.2 K). Detailed results are presented in Table 2 and a comparison of the present results with the literature data is given in Fig. 3. One can see that the agreement is satisfactory.

## 6. Conclusions

A set-up based on transitionometric principles has been designed for direct measurements of high pressure expansion of gases. A new method of calibration was presented for pressure-controlled calorimeters working with open mass calorimetric vessels. The new method of calibration is based on heat capacity standards and thus is complementary to the previous methods based on thermal expansion standards. The calibrations performed with the new method using a number of heat capacity standards demonstrated that the calibration constant of correctly designed calorimetric vessels does not depend on pressure, what is an independent confirmation of previous observations collected on calibration with the high pressure expansion of liquids. The results of test measurements with nitrogen performed in agreement with the thermodynamic foundations of the method are in satisfactory agreement with the literature data.

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