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The Construction and Testing of a New Apparatus with Knudsen Effusion Method Designed for Low Vapor Pressure Measurements of POPs

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A new apparatus with Knudsen effusion method especially designed for the vapor pressure measurements of dioxin congeners and other POPs is described. Crystalline benzoic acid was used to test the new designed apparatus. The vapor pressure and enthalpy results of the reference compound were found in good agreement with accepted literature data, even when using a small Knudsen cell for toxicity compounds in this study.

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Keyword: vapour pressure, Knudsen effusion method, enthalpy of sublimation, benzoic acid

1. Introduction

There are several methods to measure a low vapor pressure, such as gas saturation method, Knudsen effusion method and vapor pressure balance method. The Knudsen effusion method is one of the most accurate methods for measuring vapor pressures of low-volatility substances. Knudsen effusion method has long been employed for determining low vapor pressures. There are a large number of references on determining the vapor pressures of low-volatility materials include organic compounds by using Knudsen effusion method.

Vapor pressure is a very important physico-chemical parameter for predicting the behavior of Persistent Organic Pollutants (POPs) in the environment. The extremely low vapor pressures of some POPs such as PCDD/Fs lead to difficulties in measurement and cause 2~3 orders of magnitude difference among various literatures.¹⁾

A new apparatus with Knudsen effusion method especially designed for the vapor pressure measurements of dioxin congeners and other POPs is presented, and the apparatus was tested with reference compounds.

2. Principle of Knudsen Effusion Method

The theoretical background of Knudsen effusion method is the Kinetic Theory of Dilute Gases from which Knudsen²⁾ derived an equation for the vapor flow effusing through the orifice of a cell.

The sample whose vapor pressure is to be measured is placed in a container known as a Knudsen cell. The Knudsen cell is cylindrical with a small orifice in the centre of the lid. The cell is maintained at a constant temperature in an evacuated space. Effusion through the orifice gives a molecular beam that spreads out in isotropic distribution over a sphere (known as the "cosine law"). The measurement of the weight loss ΔW (kg) in a specified period of time t (s) at a constant temperature T (K) enable us to evaluate the vapor pressure by using the effusion formula 1.^{3), 4)}

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$$p_k = \frac{1}{K_c A_0} \frac{\Delta W}{t} \sqrt{2\pi RT / M} \quad (1)$$

where p_k (Pa) is the vapor pressure near the orifice, K_c is the Clausing factor, A_0 (m^2) is the area of the orifice, M (kg/mol) is the molecular weight of the effusing vapor, R ($8.314 J/mol K$) is the gas constant. Accurate K_c could be found in literatures.³⁾

For the high pressure limit to this method, Knudsen proposed that a formula equivalent to equation (1) was accurate within the precision of his measurements for $\lambda/D > 10$, where λ is the mean free path and D is the orifice diameter. The quantity λ/D is often referred to as the Knudsen number. However, subsequent workers didn't agree with on the upper limit, but generally recommended the Knudsen number between 1 and 10. The mean free path at best is only a qualitative summary of the extent of gas phase interactions.⁴⁾

The Knudsen cell, because of the continuous loss of vapor through the orifice, is not really an equilibrium system. The vapor pressure p_k calculated from rate of effusion may thus be less than the equilibrium pressure p_{eq} that a substance would exhibit in a completely closed system. Using different approaches, Whitman⁵⁾ and Motzfeldt⁶⁾ both have arrived at the result that the measured pressure p_k is related to the equilibrium vapor pressure p_{eq} by

$$p_{eq} = p_k \left[1 + \frac{K_c A_0}{A_s} \left(\frac{1}{\alpha} + \frac{1}{W'} - 2 \right) \right] \quad (2)$$

for a cylindrical cell with orifice area A_0 and Clausing factor K_c , evaporating sample area A_s , and vaporization coefficient α . The factor W' is the Clausing coefficient for the cell itself, $W' = D/2H$.

For a Knudsen cell in which height equals diameter, that $W' = 0.5$, and Whitman-Motzfeldt equation can be rewritten as

$$p_{eq} = p_k [1 + K_c A_0 / (\alpha A_s)] \quad (3)$$

If $A_0 / (\alpha A_s) \ll 1$, $p_{eq} \approx p_k$. For typical Knudsen cell dimensions, $A_0/A_s < 0.01$ and for $\alpha \approx 1$, the experimental error is great enough to mask the difference between p_{eq} and p_k . This study thereby employed equation (1) to evaluate vapor pressure of samples.

3. The Vacuum of the System Required

Knudsen effusion method requires high vacuum outside the cell due to the Knudsen number requirement. How high vacuum does it exactly need for this apparatus?

In case of measuring the vapor pressure of octachlorodibenzo-*p*-dioxin (OCDD) by this apparatus, calculations of the system vacuum required by using kinetic theory of gases is as following.⁷⁾

OCDD ($C_{12}Cl_8O_2$), molecular weight is 459.6 and molecular radius is 1.5×10^{-9} m. Assuming the vapor pressures of OCDD at 298K and 398K are 1.1×10^{-10} Pa and 5.1×10^{-4} Pa, respectively.

(1) If there is no other residual gas in the Knudsen cell, then the mean free paths of OCDD vapor at 298K and 398K are

$$\lambda_{298K} = \frac{kT}{\sqrt{2}\sigma p} = \frac{(1.381 \times 10^{-23}) \times 298}{\sqrt{2} \times (3.14 \times (1.5 \times 10^{-9})^2) \times (1.1 \times 10^{-10})} = 3.745 \times 10^6 \text{ m}$$

$$\lambda_{398K} = \frac{kT}{\sqrt{2}\sigma p} = \frac{(1.381 \times 10^{-23}) \times 398}{\sqrt{2} \times (3.14 \times (1.5 \times 10^{-9})^2) \times (5.1 \times 10^{-4})} = 1.079 \text{ m}$$

(2) In fact, there is residual air in the cell. Assuming the residual gas is nitrogen (N_2), and the pressure of the residual gas in the cell was 1 Pa at 298K, the radius of N_2 molecules is 1.08×10^{-10} m, the radius of mix gas is: $r = (r_{\text{nitrogen}} + r_{\text{OCDD}})/2 = (1.08 \times 10^{-10} + 1.5 \times 10^{-9})/2 = 8.04 \times 10^{-10}$ m,

Then the mean free path at 298K is

$$\lambda_{298K}^{\text{actual}} = \frac{kT}{\sqrt{2}\sigma p} \approx \frac{(1.381 \times 10^{-23}) \times 298}{\sqrt{2} \times (3.14 \times (8.04 \times 10^{-10})^2) \times (1 + 1.1 \times 10^{-10})} = 1.43 \times 10^{-3} \text{ m}$$

(3) How high vacuum of the system is needed?

According to the upper pressure limit of Knudsen effusion method, the Knudsen number had better be greater than 10. Assuming the diameter of the orifice in the Knudsen cell was 0.2 mm, to obtain $\lambda/D \geq 10$, it requires $\lambda \geq 2$ mm, then the total pressure in the cell at 298K should be

$$p_{\text{Total}} = \frac{kT}{\sqrt{2}\sigma\lambda} \leq \frac{(1.381 \times 10^{-23}) \times 298}{\sqrt{2} \times (3.14 \times (7.54 \times 10^{-10})^2) \times (2 \times 10^{-3})} = 0.82 \text{ Pa}$$

The total gas pressure in the cell should be less than 0.82 Pa. In other words, the vacuum of the system at 298K had better be less than 0.82 Pa.

4. Apparatus and Procedure

A new apparatus with Knudsen effusion method especially designed for the vapor pressure measurements of dioxin congeners and other POPs is shown in Figure 1.

Due to high toxicity and high costly, the sample amount used in each experiment has to be as small as possible, and therefore the size of Knudsen effusion cell should be made as small as feasible.

The sample was first ground into powder, and then charged and compressed in a thin layer on the bottom of the Knudsen effusion cell 9, so as to get a flat surface and a good heat transfer. After charging sample, the Knudsen cell 9 was hermetically sealed by a special presser, and was hung on the hook of a calibrated microbalance 1 (METTLER TOLEDO MX5 Microbalance) through a long aluminum chain at the center of the Pyrex tube 8. The Pyrex tube 8 has a length of 600mm and internal diameter of 14mm. The precision of the

calibrated microbalance 1 is of 1 microgram. A high vacuum (less than 10^{-2} Pa) of the system was established by a rotary pump 4 (DUO 2.5A, Balzers) and a turbo molecular pump 5 (TCP Balzers). Weight loss was continuously collected by the data system 10 on line. A ionization vacuum gauge 3 connect to the high vacuum chamber 4 was used to measure the vacuum of the system.

The High accuracy oil bath 7 (THERMO OH-16, TAITEC Co. Ltd, Japan) can maintain a constant temperature with an accuracy of ± 0.03 - 0.1 K in the temperature range of 298K to 523K. The accuracy of the effusion cell temperature is of paramount important, so the temperature at the cell hanging position was measured by a calibrated platinum resistance thermometer 6. Because of high vacuum of the system, it was found that the temperature at the cell hanging position is always lower than the temperature of the oil even after thermal equilibration, although the cell was deeply submerged in the large oil bath.

The effusion cell was showed in Figure 2 in detail. Vapor effusion through the small orifice at the lid of the cell gives a molecular beam that spreads out in an evacuated space.

The Knudsen effusion cells designed are composed of lids and bodies as small as feasible because of the high toxicity of POPs, which will be treated in this study. All lids and bodies are made of aluminum sheet of 0.1 mm thickness. The size of the lids is 4.4 mm in internal diameter, 2.2 mm in internal depth. The size of the bodies is 4.4 mm in

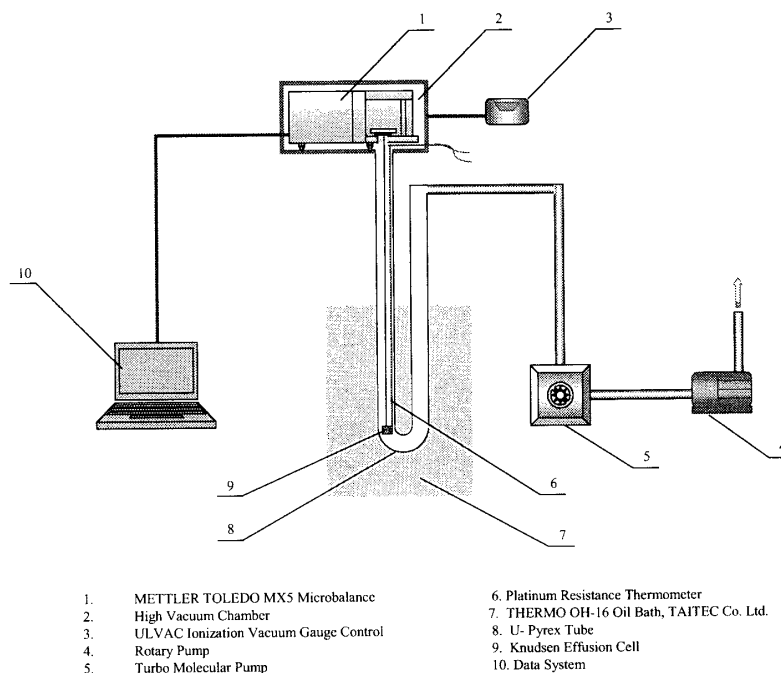


Fig 1. Apparatus schematic for vapor pressure measurements of POPs

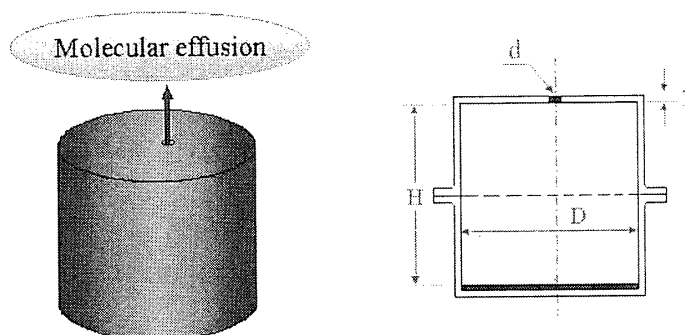


Fig 2. Scheme of Knudsen effusion cell

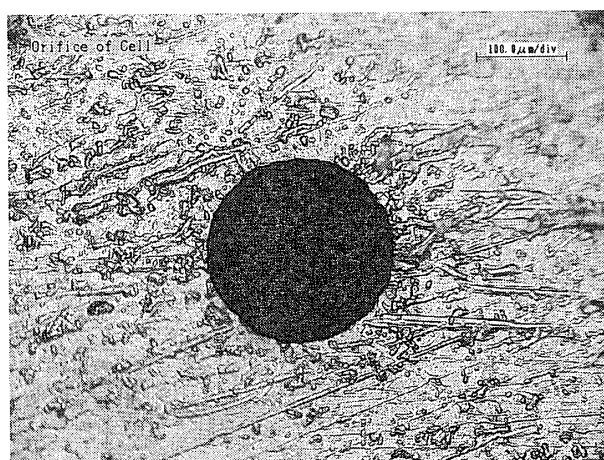


Fig 3. Micrograph of effusion orifice of Knudsen cell

internal diameter, 2.3 mm in internal depth. Both the lid and body have a fringe of 5.0 mm in diameter. There was an effusion orifice coaxially located at the lid. Different types of orifice diameter were attempted: 0.05 mm to 0.20 mm. The actual diameters and areas of the orifices were measured under a microscope with 1000 times amplification (Fig 3.). After charging sample, a lid and a body were hermetically pressed together on the fringes by a special presser. After sealing, the internal height of the cell is nearly equal to the diameter of the cell.

5. Results and discussion

Benzoic acid is recommended as reference materials for the measurements of low vapor pressure and sublimation enthalpy.⁸⁾ This study employed benzoic acid to test the performance of the apparatus described above.

Vapour pressure Measurements of benzoic acid with the present apparatus were made in the temperature range of 299K to 328K using three cells. The thickness of each cell was 0.10mm, and orifice area of each cell and corresponding Clausing factor K_c given by Cater³⁾ are list in Table 1.

Table 1 Vapor pressure results of benzoic acid

Exp. No.	Cell No.	Orifice area (10^{-6}mm^2)	K_c	T (K)	Time(s)	Sublimated mass (mg)	Vapor pressure (Pa)
1				299.15	3590	0.027	0.13
2				303.25	3630	0.047	0.22
3				308.15	3613	0.083	0.39
4	Cell 1	31430.9	0.672	313.15	3615	0.143	0.69
5				318.15	3640	0.241	1.16
6				323.15	3630	0.388	1.88
7				328.15	3627	0.615	3.01
8				303.25	3600	0.027	0.18
9				308.15	3600	0.058	0.40
10	Cell 2	23006.6	0.638	313.15	3640	0.103	0.71
11				318.15	3650	0.174	1.20
12				323.15	3631	0.288	2.01
13				328.15	3632	0.463	3.26
14				303.25	3600	0.027	0.21
15				308.15	3640	0.046	0.36
16	Cell 3	20033.2	0.641	313.15	3630	0.082	0.64
17				318.15	3610	0.139	1.11
18				323.15	3600	0.229	1.84
19				328.15	3602	0.375	3.04

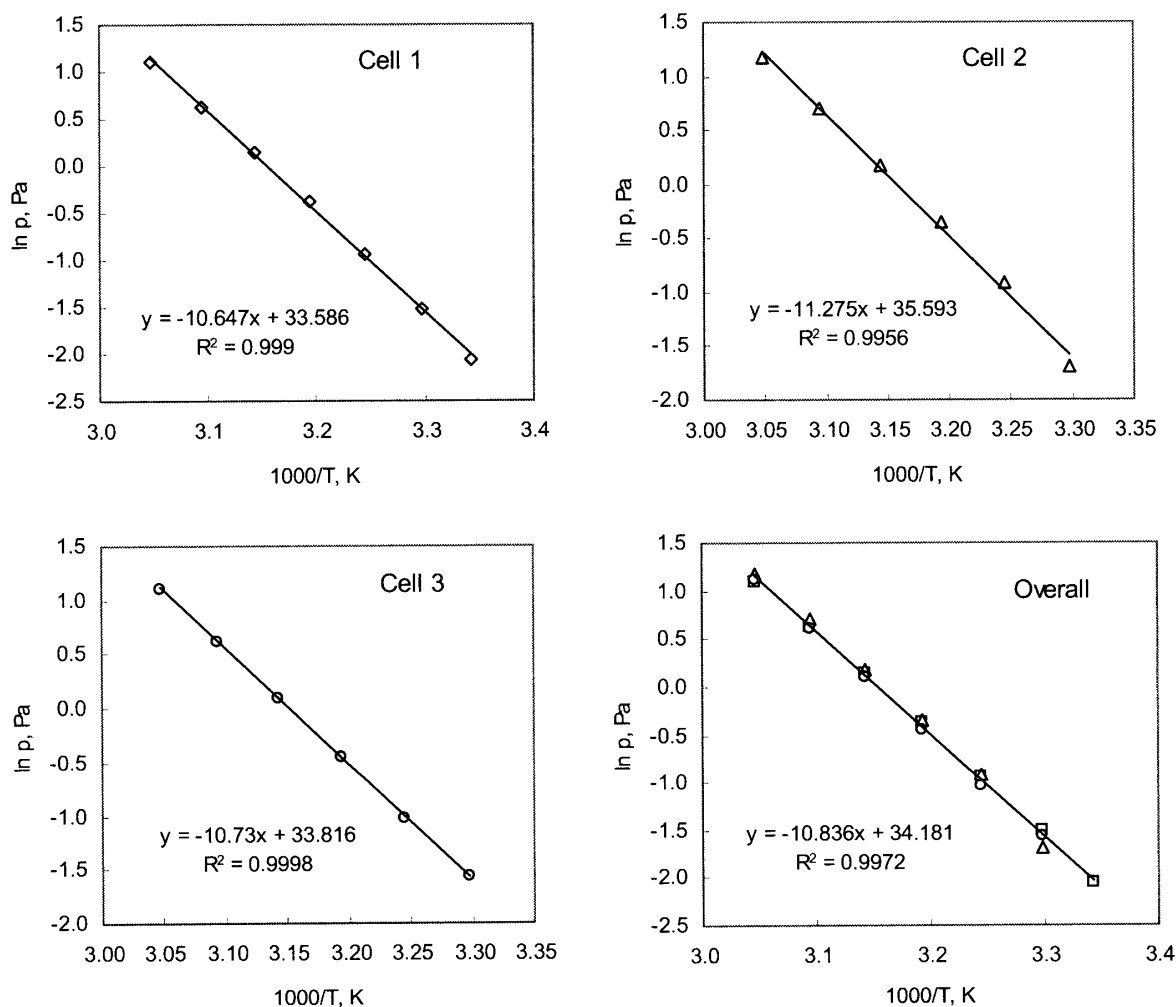
The sublimation enthalpy of the sample can be obtained using the Clausius-Clapeyron equation (4).

$$\ln p = -(\Delta_{\text{sub}}H/R)/T + \Delta_{\text{sub}}S/R \quad (4)$$

The experimental results of benzoic acid were plotted into a natural logarithm of vapor pressure ($\ln p$) vs. $1/T$ for each cell and also for overall treatment of all data (Fig.4), the slope of the straight line was $\Delta_{\text{sub}}H/R$.

Table 2 Sublimation enthalpies of benzoic acid.

Reference	Temperature range (T/K)	$\ln(p/\text{Pa}) = a - b \cdot 10^3 \cdot (K/T)$		$\Delta_{\text{sub}}H(T)$ (kJ · mol ⁻¹)
		a	b	
This study, Cell 1	299-328	33.586±0.487	10.647±0.152	88.52±1.26
This study, Cell 2	303-328	35.593±1.185	11.275±0.374	93.74±3.11
This study, Cell 3	303-328	33.586±0.487	10.731±0.072	89.21±0.60
This study, Overall	299-328	34.181±0.446	10.836±0.140	90.09±1.16
J. Sachinidis and J.O. Hill, 1980 ¹⁰⁾	333-393	32.622	10.262	85.32
C.G. De Kruif and J.G. Blok, 1982 ¹¹⁾	316-391	34.038	10.803	89.82
M. Colomina <i>et al</i> , 1982 ¹²⁾	293-313	34.231	10.867	90.35
S. Murata <i>et al</i> , 1982 ¹³⁾	320-370	32.933	10.366	86.18
E. Kaisersberger <i>et al</i> , 1985 ¹⁴⁾	273-330	36.07±0.48	11.441±0.140	95.1±1.8
O.T. Glukhova <i>et al</i> , 1985 ¹⁵⁾	293-319			90.8±0.6
M.A.V. Ribeiro da Silva and M.J.S Monte, 1990 ¹⁶⁾	307-314	33.601±0.330	10.669±0.102	88.70±0.85
M.A.V. Ribeiro da Silva <i>et al</i> , 1995 ¹⁷⁾	304-317	34.320±0.302	10.886±0.100	90.51±0.83
M.A.V. Ribeiro da Silva <i>et al</i> , 1995 ¹⁷⁾	304-317	33.930±0.302	10.753±0.100	89.40±0.83
M.A.V. Ribeiro da Silva <i>et al</i> , 1995 ¹⁷⁾	316-390	34.038±0.051	10.803±0.018	89.82±0.15
M.A.V. Ribeiro da Silva <i>et al</i> , 1995 ¹⁷⁾	279-295	34.146±0.114	10.819±0.033	89.95±0.27
R. Sabbah <i>et al</i> , 1999 ⁸⁾	298.15			89.700±1.000

**Fig 4.** Temperature dependence of benzoic acid vapour pressure with different cell

The enthalpy and entropy of sublimation obtained by this method referred to the mean values in the experimental temperature range. The sublimation enthalpy results obtained for individual cell and overall are given in Table 2.

Fig 4 shows there is no significant variation of vapor pressure values measured with different orifice sizes, which might mean the vaporization coefficient α is close to 1, and the measured vapor pressure values are nearly equal, within experimental error, to the equilibrium vapor pressure p_{eq} .

The vapor pressure and sublimation enthalpy of benzoic acid have been measured by a variety of different techniques and investigators. For comparison, the vapor pressure and sublimation enthalpy results reported since 1980 are also listed in table 2. The standard molar sublimation enthalpy of benzoic acid determined by this work in the experimental temperature range ($90.09 \pm 1.16 \text{ kJ} \cdot \text{mol}^{-1}$) agrees, within experimental error, with the value of $89.70 \pm 1.00 \text{ kJ} \cdot \text{mol}^{-1}$ recommended by Cox⁹⁾ and Sabbah *et al*⁸⁾.

6. Conclusion

The vapor pressure and sublimation enthalpy results of benzoic acid measured with the present apparatus are in good agreement with accepted literature data, even when using a small Knudsen cell for toxicity compounds in this study.

The testing results of the compound give us confidence in the present apparatus, which has the advantages of accurate online mass loss determination, different temperature measurements within an experiment, and smaller sample amount and shorter experimental time than other such studies.

References

- 1) W.Y. Shiu and K.C. Ma, *J. Phys. Chem. Ref. Data*, Vol. 29 (2000), 387-462.
- 2) M. Knudsen, *Ann. Phys.*, 34(1911), 593.
- 3) E. D. Cater, Ch.2A, *Physicochemical Measurements in Metals Research*, Part 1, R. A. Rapp, Ed., John Wiley, New York, 1970.
- 4) K. D. Carlson, Ch.5, *The characterization of High-Temperature Vapors*, J. L. Margrave, Ed., Wiley, New York, 1967.
- 5) C. J. Whitman, *J. Chem. Phys.*, 20(1952), 161.
- 6) K. Motzfeldt, *J. Phys. Chem.*, 59(1955), 139.
- 7) P. W. Atkins, *Physical Chemistry*, Oxford University Press, 1978, ISBN 0198551479.
- 8) R. Sabbah, X.W. An, J.S. Chickos, M.L.P. Leitao, M.V. Roux and L.A. Torres: *Thermochim. Acta* 331 (1999) 93-204.
- 9) J.D. Cox, *Pure Appl. Chem.*, 40(1974), 424.
- 10) J. Sachinidis and J.O. Hill, *Thermochim. Acta* 35 (1980) 59-66.
- 11) C.G. De Kruif and J.G. Blok: *J. Chem. Thermodynamics* 14 (1982) 201-206.
- 12) M. Colomina, P. Jimenez and C. Turrion: *J. Chem. Thermodynamics* 14 (1982) 779-784.
- 13) S. Murata, M. Sakiyama and S. Seki: *J. Chem. Thermodynamics* 14 (1982) 723-731.
- 14) E. Kaisersberger, W. Hardrich and W.D. Emmerich: *Thermochim. Acta* 95 (1985) 331-336.
- 15) O.T. Glukhova, N.M. Arkhangelova, A.B. Teplitsky, L.F. Sukhodub and I.K. Yanson: *Thermochim. Acta* 95 (1985) 133-138.
- 16) M.A.V. Ribeiro da Silva and M.J.S. Monte: *Thermochim. Acta* 171 (1990) 169-183.
- 17) M.A.V. Ribeiro da Silva, M.J.S. Monte and J. Huinink: *J. Chem. Thermodynamics* 27 (1995) 175-190.