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having a chemical composition of 4.4wt% Mg–0.7wt% Mn–0.15wt% Cr with the balance as Al. An aluminum 5083 alloy was processed by equal channel angular pressing at 473 K to produce an ultra fine grain size of ∼ 300 nm. Aluminum 5083 was deformed by ECAP following Route Bc up to 8 passes at 473 K. The grain size was changed from about 200 mm to ∼300 nm by deformation. The specific heat capacity was measured from 100 K to 800 K using the differential scanning calorimeter (DSC) and the heating rate was 10 K/min in an argon atmosphere. The specific heat capacity were increased to the monotonically with temperature rise, but high temperature region about 800 K was a little different passes of ECAP. The DSC curves are corresponds to the precipitation sequences: decomposition of saturated solid solution, formation and dissolution of Guinier-Preston zones, transition phase, precipitation equilibrium phase.

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The Volatility Of Solid Perfluorocarboxylic Acids

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The accumulation of perfluorocarboxylic acids (PFCA) in the biota of even remote places like the arctic, is now considered to be an emerging global environmental problem [Silva, 2004] resulting in new tasks for the determination of the physical-chemical properties of these compounds as well as new challenges for chemical regulators and environmental fate modelers.

For perfluorocarboxylic acids, only very few data on the vapour pressures of the liquid phase are available in the literature [Kaiser, 2005], and for solid PFCA only some estimations of the vapour pressures were reported. In this work, the volatility of a series of linear perfluorocarboxylic acids [perfluoroheptanoic acid (CN=7) to perfluorododecanoic acid (CN=12)], was studied.

The enthalpies of sublimation of the six compounds were measured using the Vacuum Drop Calvet Microcalorimetry method [Santos, 2004], while the solid vapour pressures were measured using a high accuracy static apparatus based on a MKS Baratron capacitance diaphragm pressure sensor [Monte, 2006].

The gas phase heat capacities and the dimerisation equilibria were studied by DFT at the B3LYP/6–311++G(d,p) level of theory.

The results obtained will be used in order to interpret the unexpected high volatility of the PFCA.

References

[1] Kaiser, M. A.; Larsen, B. S.; Kao, C.-P. C.; Buck, R. C., J. Chem. Eng. Data, 50 (2005) 1841.
[2] Monte, M. J. S.; Santos, L. M. N. B. F.; Fulem, M.; Fonseca, J. M. S.; Sousa, C. A. D., J. Chem. Eng. Data, 51 (2006) 757.
[3] Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M.A. V. , Thermochim. Acta, 415 (2004) 15.
[4] Silva, A. O.; Mabury, S. A., Environ. Sci. Technol., 38 (2004) 6538.

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Thermal stability, sublimation pressures and diffusion coefficients of some organometallic compounds

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Organometallic compounds with low but observable vapour pressures are interesting for several applications. One of these is the chemical vapour deposition (CVD), which is an actual field. For this process the precursor molecules (which often are metal acetylacetonates) are evaporated. To engineer such a process the knowledge of the vapour or sublimation pressures is essential because they determine the maximum theoretical growth rate and the composition. The gaseous diffusion coefficients are needed for the calculation of the Sherwood and Lewis numbers used to describe mass transfer process. Such data are often either lacking or not well established.

We have started a program to study the long term thermal stability, sublimation pressures and the diffusion coefficients of organometallic compounds. Recently [1], we demonstrated a method for the evaluation of diffusion coefficients of less volatile substances

THE VOLATILITY OF SOLID PERFLUOROCARBOXYLIC ACIDS

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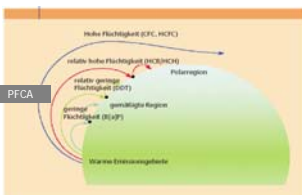
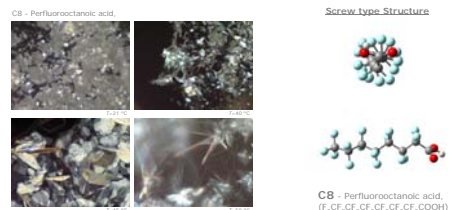Luis M. N. B. F. Santos, LBSANTOS@FC.UP.PT

INTRODUCTION / AIM

□ The accumulation of perfluorocarboxylic acids (PFCA) in the biota of even remote places like the arctic, is now considered to be an emerging global environmental problem [Silva, 2004] resulting in new tasks for the determination of the physical-chemical properties of these compounds as well as new challenges for chemical regulators and environmental fate modelers.

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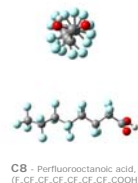
PFCA's

Global distillation and fractionation

Source: Chem. Unserer Zeit, **2007**, 41, 276 – 284

C8 - Perfluorooctanoic acid.

Screw type Structure

C8 - Perfluorooctanoic acid, ($F_3CF_2CF_2CF_2CF_2CF_2CF_2COOH$)

EXPERIMENTAL

Static Apparatus: Absolute Capacitance Manometer

□ The vapour pressures of the six perfluorocarboxylic acids were measured using the Static apparatus recently described in the literature [Monte, 2006].

□ The Static apparatus, is based on a absolute (MKS Baratron 631A) type capacitance diaphragm manometer, enables the measurement of vapour pressures in the pressure range (0.4 – 133) Pa and (0.4 – 1333) Pa and temperature range (243 to 473) K.

□ The temperature of the sample is measured using a platinum resistance thermometer Pt100 class 1/10. The thermometer was calibrated by comparison with a SPRT, Tinsley, 5187A.

Calvet Microcalorimetry

□ The standard ($p^o = 10^5$ Pa) molar enthalpies of sublimation of the six compounds were measured by Calvet Microcalorimetry, model SETARAM HT 1000, using a similar technique of the drop-method. The measuring procedure and the performance of the apparatus is described in the literature [Santos, 2004]. Samples of about 3-9 mg of each compound were placed into thin capillary tubes and were dropped simultaneously with the corresponded blank tube at room temperature into the hot reaction zone of the calorimeter.

□ The standard molar enthalpy of sublimation at T = 298.15 K was calculated from the experimental value of at the temperature T of the hot zone based on the following hypothetical thermochemical diagram:

$$\Delta_{cr}^g H_m^o (T = 298.15K) = \Delta_{cr,298.15\,K}^{g,T} H_m - \Delta_{298.15\,K}^{T} H_m^o (g)$$

Vacuum
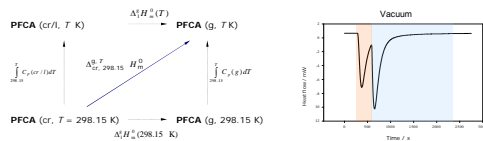
□ In where, the $\Delta_{298.15K}^{T} H_m^o (g)$ represents the molar enthalpic correction for the respective heat capacity of the gaseous phase.

Computational Chemistry

□ The molar enthalpic correction for the respective heat capacity of the gaseous phase, was calculated by computational thermochemistry at B3LYP/6-311++G(d,p) using the frequency scaling factor of 0.9688.

□ Computational chemistry was also used to evaluate the total screw rotation angle. The geometry optimization of each perfluorocarboxylic acid was calculated at BP86/TZVP level o theory.
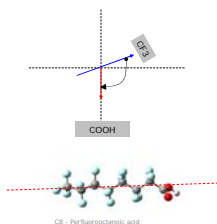
Screw rotation angle /°	
C7	68
C8	85
C9	104
C10	119
C11	138
C12	155

Ab-initio Geometry Optimization at BP86/TZVP level

C8 - Perfluorooctanoic acid

REFERENCES

Kaiser, M. A.: Larsen, B. S.: Kao, C.-P. C.: Buck, R. C., J. Chem. Eng. Data, 50 (2005) 1841.
Monte, M. J. S.: Santos, L. M. N. B. F.: Fulem, M.: Fonseca, J. M. S.: Sousa, C. A. D., J. Chem. Eng. Data, 51 (2006) 757.
Santos, L. M. N. B. F.: Schröder, B.: Fernandes, O. O. P.: Ribeiro da Silva, M.A. V. , Thermochim. Acta, 415 (2004) 15.
Silva, A. O.: Mabury, S. A., Environ. Sci. Technol., 38 (2004) 6538.

INSTRUMENTATION

Static Apparatus

Pressure drift: 0.1 mPa/s

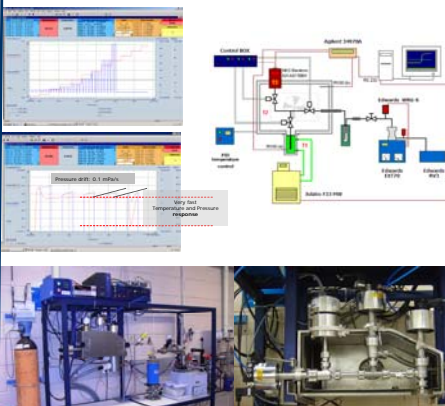Very fast Temperature and Pressure **response**

Figure 2 – Pictures and schematic representation of Static Apparatus based on a MKS absolute capacitance diaphragm manometer and details of the data adquisition software.

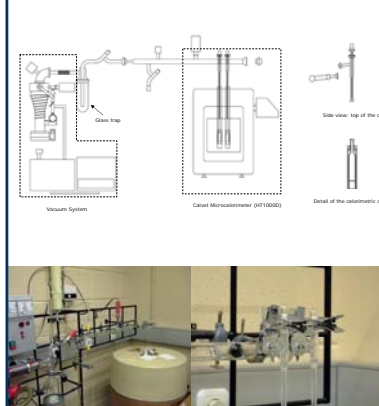### Calvet Microcalorimetry Drop Method

Side view: top of the cell

Vacuum System   Calvet Microcalorimeter (HT10000)   Detail of the calorimetric cell

Figure 3 – Picture and schematic representation of Calvet Microcalorimeter HT1000 and the vacuum line.

RESULTS AND DISCUSSION

Static apparatus
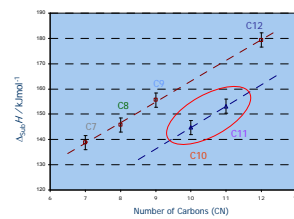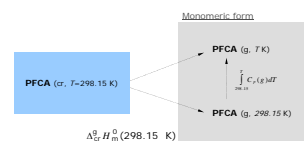**Vapour Pressure measurements**

Monomer → Dimer

$PFCA$ (cr, T K) → $\Delta_{cr}^g G_m^o (T K)$ → $PFCA$ (g, T K) → $\Delta_{dim} G_m^o (g)$ → ½ ($PFCA$)$_2$ (g, T K)

..... **ODD-EVEN effect**

298.15 K   273.15 K

200 Pa   C7
C8   C9
50 Pa   C11
C10
10 Pa   C12
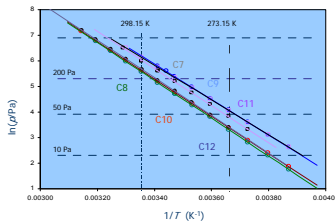
Calvet Microcalorimetry drop Method
Enthalpies of sublimation

Monomeric form

$PFCA$ (g, T K)

$PFCA$ (cr, T=298.15 K) $\int C_p(g) dT$

$PFCA$ (g, 298.15 K)

$\Delta_{cr}^g H_m^o$ (298.15 K)

C12
C9
C8
C7   C11
C10

Number of Carbons (CN)

□ The results obtained for the volatility of the series of linear perfluorocarboxylic acids [perfluoroheptanoic acid (CN=7) to perfluorododecanoic acid (CN=12)] show a marked ODD and EVEN effect.

□ An unexpected high volatility and identical vapour pressure in the ODD and EVEN series perfluorocarboxylic acids.

□ The enthalpies of sublimation obtained by calorimetric direct measurements, follows an interesting pattern, in where the results obtained for the CN=10 (perfluorodecanoic) and CN=11 (perfluoroundecanoic) are falling down from the regular increase of the series (CN=7 : 8: 9 : 12).

□ Powder diffraction X-ray data at different temperatures and DSC data, indicates a very complex semi-crystalline structure of the perfluorocarboxylic acids.

□ The study of the dimerization equilibrium in the gaseous phase, at different temperatures, of perfluorocarboxylic acids by Ab-initio is in progress.

□ The vapour liquid equilibrium will be compared with the COSMOS-RS predictions.