ISOCHORIC SPECIFIC HEAT OF SULPHUR HEXAFLUORIDE AT THE CRITICAL POINT A SPACELAB EXPERIMENT FOR THE GERMAN D1-MISSION IN 1985

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ABSTRACT

The mechanical and functional concept of a space qualified scanning ratio calorimeter is presented for measuring the isochoric specific heat of SF_6 near the critical point. The micro-gravity relevance of this experiment is discussed and underlined by laboratory measurements, the hydrostatic height of the specimen being varied. In 1-g reference experiments the critical exponent and parameters for c_V have been determined. Critical relaxation effects are taken into account by a suitable functional time profile for the HPT spacelab experiment.

Keywords: Critical phenomena, micro-gravity, critical exponents, isochoric specific heat, scanning ratio calorimeter, Spacelab, D1-mission

1. INTRODUCTION

Studies of critical phenomena have grown to a considerable field in theoretical physics. In the recent years a global theory, the "renormalization group" has focused great expectations of scientists, for it predicts macroscopic thermodynamic properties around critical points without considering the molecular structure of the system to be investigated. This theory is applicable to physically different kinds of critical phenomena such as magnetisation of a solid body near the Curie Point as well as phase separations of binary mixtures or phase changes of pure liquids near critical temperature. The universality of this model has gained importance since up to the present day it has not been possible in most cases to describe the macroscopic behaviour including phase transitions out of molecular interaction using methods of statistical physics. However, the range in which the renormalization group holds is confined to a small region around critical points. This region is characterized such that macroscopic properties can be expressed in terms of simple power laws. For example the specific heat at constant volume c_V becomes

$$c_V/R = A\left|\frac{T-T_c}{T_c}\right|^{-\alpha} + B \qquad (1)$$

where R denotes the gas constant, T_c the critical temperature and A, α and B parameters for which theoretical calculation yield numerical values.

Terrestrial investigations have been performed that show a reasonably good agreement of the experimentally determined parameters in Eq. (1) with the corresponding theoretical results. Unfortunately, like in many other measurements at fluid critical states, these results suffer from gravitational influences that enhance their dominating significance just at the critical point, the target of all experimental efforts.

The D1-Mission in 1985 will open an opportunity to perform longterm c_V-measurements under micro-gravity (μ-g) conditions. It will supply data free from systematic errors induced by gravitational effects. For this purpose a space qualified calorimeter has been developed which is housed in a <u>h</u>igh <u>p</u>recision <u>t</u>hermostate ("HPT") and integrated in the MEDEA-rack of the spacelab.

2. EXPERIMENTAL PROBLEMS AND MICRO-GRAVITY RELEVANCE

The experimental determination of the parameters A, α and B in the equation (1) for the isochoric specific heat c_V is inhibited by the fact that the power laws describe the

behaviour of state only within a small temperature range $/\tau/ < 2*10^{-3}$ around the critical point where $\tau = (T-T_c)/T_c$ (LANGE, 1983). Therefore, experimentation near critical state requires extraordinary efforts in thermostabilization, electronic measuring and control and can be performed only in samples of small dimensions. Fluid at critical temperature is very sensitive to external fields like temperature gradients and gravity forces. The disturbing influence of gravity, however, can only be suppressed in μ-g environment since in earthbound experiments the finite hydrostatic height in the test substance cannot be sufficiently reduced to layer thicknesses of order of the largest density fluctuations to achieve critical state throughout the complete fluid volume. Therefore, 1-g results are affected by an averaging error which can merely be estimated in data evaluations (Hohenberg and Barmatz, 1972). The closer to the critical point refined experimentation techniques enable measurements, the more influences of gravitational body forces gain dominace.

Since near the critical point C.P. the isotherms in a pressure-density diagramm are almost horizontal (Fig. 1)

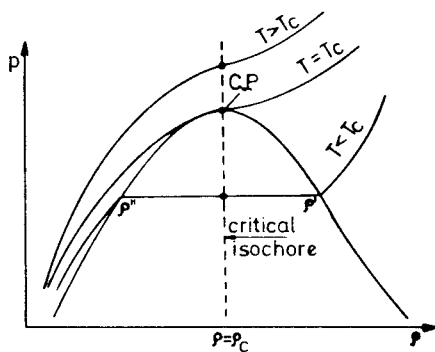

Fig. 1:   Pressure- density diagram of a pure fluid near critical state

already a small hydrostatic pressure difference

$$\Delta p = \rho gH \tag{2}$$

in the specimen of height H is sufficient to produce density profiles. In addition the isothermal compressibility

$$K_T = \frac{1}{\rho} (\partial \rho / \partial p)_T \tag{3}$$

approches infinity ($\partial p / \partial \rho = 0$) with the result that small pressure changes cause considerable density sedimentations

$$(\partial \rho / \partial h)_T = -\rho^2 K_T g (a/g) \tag{4}$$

where h is the hydrostatic length coordinate and a characterizes the actual gravitational field imposed on the fluid. These layers of different density are measurable or can be computed applying an equation of state. Fig. 2 and 3 show such density profiles under variation of temperature near its critical value. Consequently measurments of caloric properties like c_V represent integral values over all states existing in a fluid volume of finite dimensions. Gravity induced density gradients falsify measurements because these caloric properties are no more significant for a thermodynamic point of state but represent a somehow integral average.
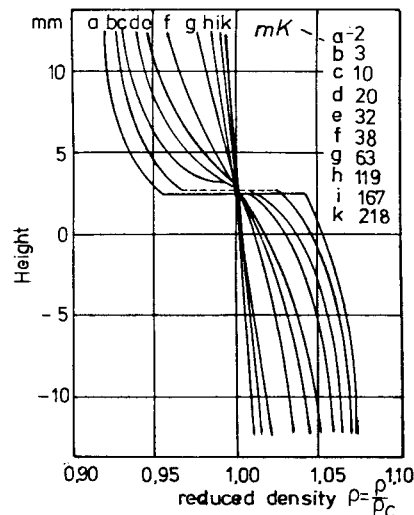

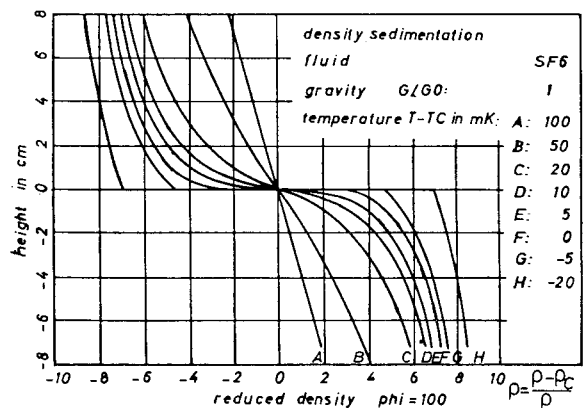Fig. 2:   Measured density sedimentation of N_2O near critical state (STRAUB, 1977)

Fig. 3:   Computed density profiles of SF_6 near critical state (LANGE, 1983)

3. EXPERIMENTAL APPARATUS

Fig. 4 and 5 show the mechanical and the corresponding functional set up of the "HPT" scanning ratio calorimeter which in principle is similar to the ones used by
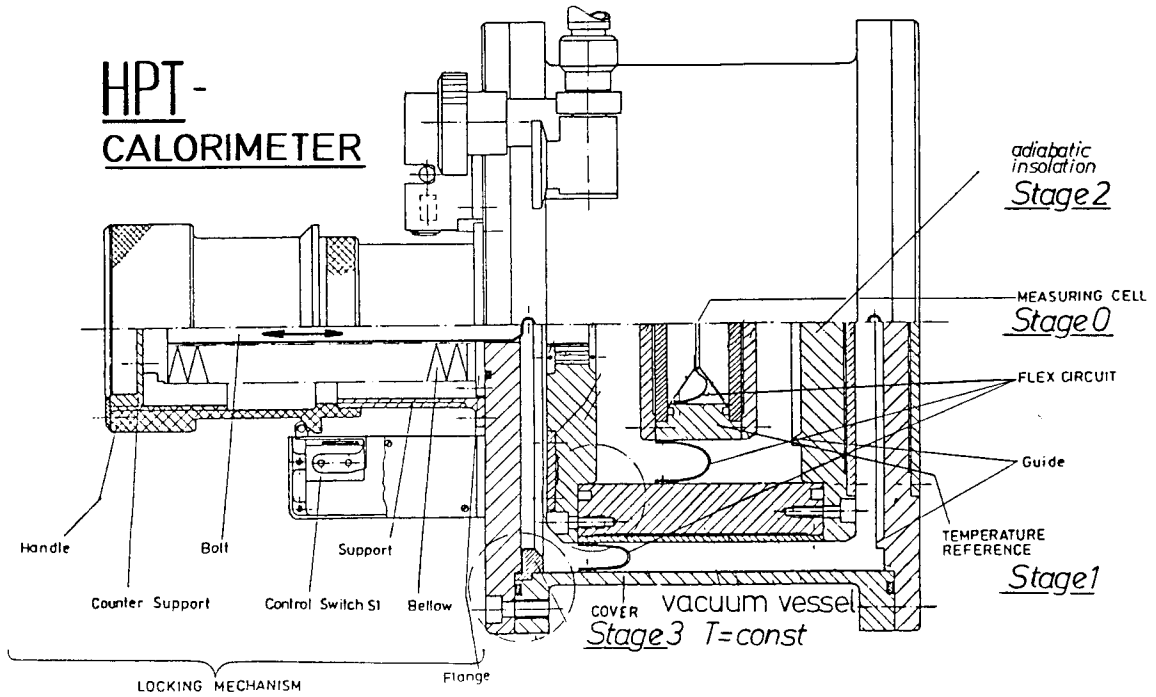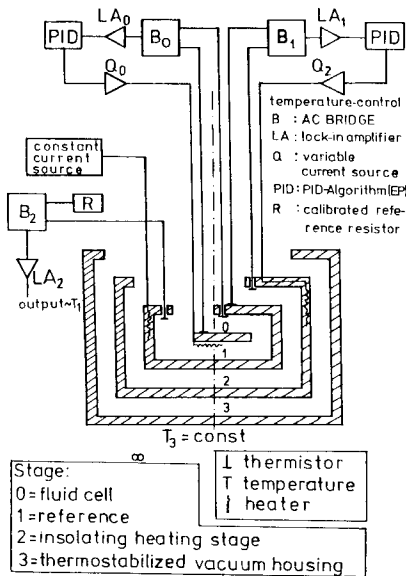
HPT-CALORIMETER

adiabatic insolation
Stage 2

MEASURING CELL
Stage 0

FLEX CIRCUIT

Guide

TEMPERATURE REFERENCE
Stage 1

Handle

Bolt

Support

Counter Support   Control Switch S1   Bellow

COVER   vacuum vessel
Stage 3 T=const

LOCKING MECHANISM   Flange

Fig. 4:   Mechanical setup of the HPT-calorimeter

LA$_0$ LA$_1$

PID ◁ B$_0$ B$_1$ ▷ PID

Q$_0$ Q$_2$

temperature-control
B : AC BRIDGE
LA : lock-in amplifier
Q : variable
      current source
PID: PID-Algorithm(EP)
R : calibrated refe-
      rence resistor

constant current source

B$_2$ R

LA$_2$
output~T$_1$

T$_3$ = const

∞

Stage:
0 = fluid cell
1 = reference
2 = insolating heating stage
3 = thermostabilized vacuum housing

thermistor
T temperature
heater

Fig. 5:   Functional diagram of the HPT calorimeter

shuttle launch. Additionally locking shortens cooling the calorimeter since heat from the center (except stage 0) transfers by conduction accross the touching vessel surfaces.

The structure of the test cell (stage 0) resembles the one used by BUCKINGHAM (1973). The design requirements to be fulfilled are: low heat capacity of the stainless steel container compared to the test substance, a sufficient mechanical resistance against an inner pressure of about 40 bar, a small hydrostatic height for preceeding 1-g reference tests. Fig. 6 shows cross sections of the coin-shaped cell.
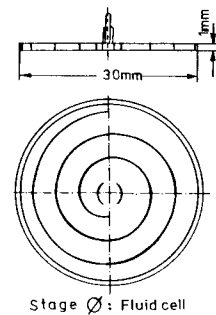
Fig. 6:
Sample cell,
calorimeter stage 0

30mm

Stage Ø: Fluid cell

BUCKINGHAM (1973) and WÜRZ (1980). The calorimeter consists of four cylindrical vessels elastically suspended in each other: the central stage 0 containing the test substance, reference stage 1 constantly heated up, stage 2 adiabatically shielding the center from the thermal environment and the vacuum vessel 3 kept at constant temperature. While turning the handle of the locking mechanism a bolt is moved along the center axis and pushes stage 1 and 2 towards 3 till they rest in guiding edges in order to prevent the suspension from being overstrained by shaking and accelerations during the

Due to the extremely reduced wall thickness a machined spiral supports the upper and the lower transverse face soldered together. Furthermore, by this means the thermal diffusion lengths are minimized and thermal equilibrium is eased.

In operation the calorimeter is evacuated to pressures of 10^{-5} mbar gained by an ion getter pump to reduce heat

leaks between the nickel plated vessels which are all electrically heated. Thermistors are used to measure temperature differences as well as to determine the overall process temperature T_1-T_c relatively to critical temperature T_c.

A constant current source supplies stage 1 with adjustable power and linearly raises the temperature T_1. The two controll loops 0 and 1 balance the temperature differences between the stages such that $T_0-T_1=0$ and $T_2-T_1=0$, respectively. Both control systems are essentually identical. They consist of an AC-bridge B to convert temperature differences between two adjacent stages into voltage signals, a lock-in amplifier LA including an oscillator and a variable current source Q. According to a PID-algorithm Q is regulated by a central processor unit that also controlls house keeping and frontpanel display. In the open loop 2 bridge B2 measures the process temperature with respect to a constant resistor R chosen such that the output signal is proportional to T_1-T_c where $T_c=45.58^\circ C$ is the critical temperatur of SF_6.

Data relevant for scientific evaluation is encoded in a 12 bit format, other parameters in 8-bit words. With a frequency of 128 byte per 0.6 sec data is transferred to an external data handling module for high rate multiplexing and is finally sent to ground for online monitoring in Oberpfaffenhofen nearby Munich. In addition a computer link between the German ground station and the laboratory of the authors at the Technical University in Munich permits quasi online data evaluation which provides a means to advise the astronauts while they manually operate the apparatus in case of disturbance or mission termination.

4.METHOD OF MEASUREMENT

The method of measurement is, very simplified, based on the fact that controllable heating the specimen (stage 0) is gained by force such that the temperature-time gradient stays constant. An energy balance applied on stage 0 and 1 yields a system of equations

$$C_0 \, (dT_0/dt) = P_0 + \dot{Q}_{01} \qquad + P_{T,0} \qquad (5)$$
$$C_1 \, (dT_1/dt) = P_1 - \dot{Q}_{01} + \dot{Q}_{12} + P_{T,1} \qquad (6)$$

where $C_0 \, (dT_0/dt)$ denotes the capacity of stage 0 times temperature ramp, P_0 the electrical heating power, $\dot{Q}_{01}$ the heat flux from 0 to 1 and $P_{T,0}$ the electrical power dissipated in the thermistor.

In the following outline the correction terms $\dot{Q}_{ij}$ and $P_{T,i}$ are neglected, i.e. it is assumed that there is no thermal coupling between the calorimeter vessels and ideal, nondissipative thermistors are used.

As stage 1 is heated with constant power P_1 its temperature rises linearly over time, the heat capacity C_1 assumed constant. Both control systems regulating cell 0 and stage 2 govern the temperatures T_0 and T_2 according the profile $T_1(t)$ such that

$$dT_0/dt = dT_1/dt = dT_2/dt. \qquad (7)$$

This controll condition combines the energy balance (5 and 6) to an explicit function of the temperature depending heat capacity of stage 0 to

$$C_0(T) = C_1 \, P_0(T)/P_1 \qquad (8)$$

with

$$C_0(T) = C_{0,container} + m_{fl.} \, c_{v,fl.}(T) \qquad (9)$$

where $c_{v,fl}(T)$ is the specific heat of the test substance to be measured versus temperature.

5. EXPERIMENTAL TIME PROFILE

In order to achieve negligible disturbances of the thermodynamic equilibrium in the fluid volume the realization of heating rates as small as possible is essential. Only if this is guaranteed the continuous method of measurement can be assumed quasi-stationary. For earthbound experiments temperature gradients of $dT/dt=10^{-6}$ K/sec still lead to the establishment of equilibrium around the critical point except within a temperatur span of $/\tau/ < 3.5*10^{-5}$ mK (LANGE, 1983). Owing to the reduced thermal diffusivity, finite spacial temperature gradients remain. However, these values of experience are superimposed by density relaxation effects which do not exist in μ-g environment. Thus reliable reference data of thermal relaxation under reduced gravity is not available yet. This information is expected from the data evaluation of the three different temperature ramps of the HPT-experiment (fig. 7).

The sample is heated up with three gradients that vary in orders of ten. 1-g reference data of the same profile will be acquired immediately after the D1-mission using the same apparatus. A comparison will reveal valuable information about pure, isolated thermal diffusion in a fluid at critical state.
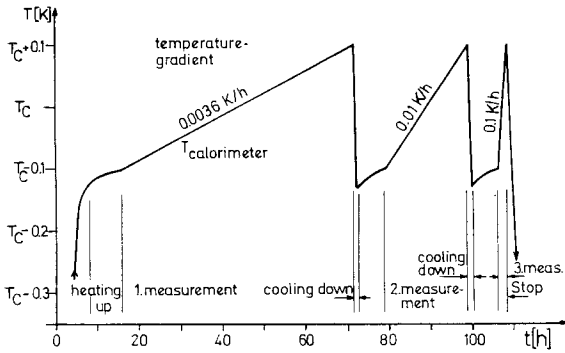
fig. 7:   Temperatur-time profile of the HPT spacelab calorimeter with three different temperature ramps (total duration of the experiment: 108 hours).
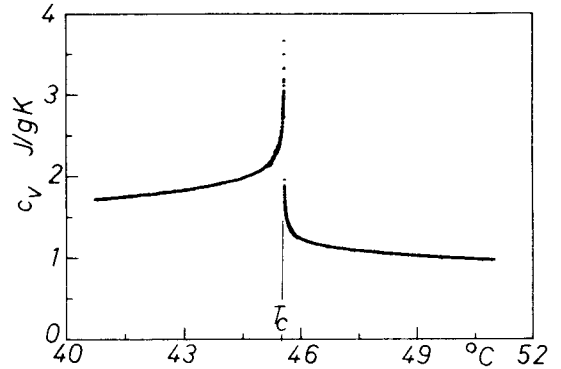
6. PRELIMINARY RESULTS

The μ-g relevance of the HPT-phase change experiment is well documented in fig. 8.
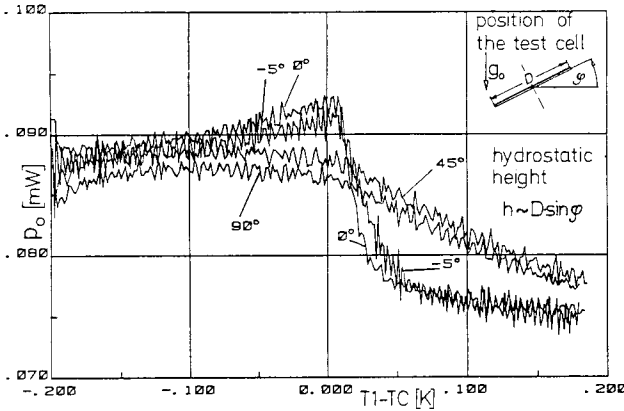

Fig. 8:   Heating power P_0 for different hydrostatic heights in the fluid cell.

For constant power input P_1 in stage 1 the controlled heating power P_0 is proportional to the specific heat $c_v(T)$ (Eq. 8 and 9). For an inclination angle $\varphi = 0°$ (minimum, 1mm, of the hydrostatic height, fig.6) the characteristic peak at $T_1-T_c=0$ reaches its maximum and deminishes as the angle grows to -5° or to +5°, respectively. For 45° or ultimately at 90° (30 mm) the enhancement vanishes completely. This data is obtained from a laboratory test of the HPT-engineering model.

In previous experiments c_v-measurements have been performed using a laboratory version of a scanning ratio calorimeter (LANGE, 1983). As can be seen in fig. 9 the behaviour of the specific heat c_v clearly exhibits a singularity at the critical temperature 45.58°C (SF₆).

Fig. 9.:   The isochoric specific heat c_v of SF₆ near the critical temperature T_c=45.58 °C.

Data fitting yields parameter values for the power equation (1)

$$c_v/R = A \left| \frac{T-T_c}{T_c} \right|^{-\alpha} + B \qquad (10)$$

with B = 2.54, α = 0.0977 and A = 10.07 in the one-phase region and A" = 18.41 for the two-phase region. These parameters are in accord with theoretically derived values (CAMP et al., 1978; BAKER et al. 1976).

The critical enhancement of c_v measured as T approaches its critical value is well represented by equation 10 as exhibited in the double logarithmic plot of fig 10.
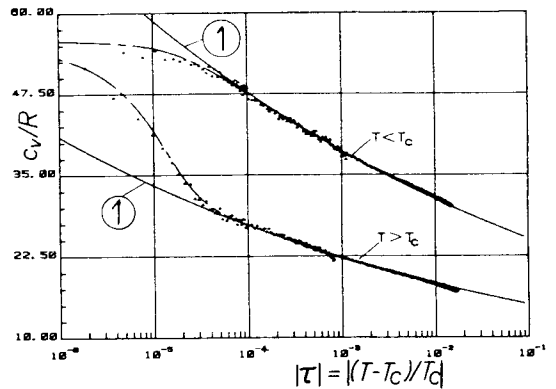

Fig. 10:   (1): curves expected for micro-gravity, the curves are extrapolated after data fitting according Eq. 10 for $3.5*10^{-5} <$ / τ / $<10^{-2}$
(2): measured curves of c_v for 1-g and 1 mm cell height

A constant exponent α leads to a linear c_v-behaviour in fig. 10 which is not the case for / τ / $<$ $3.5*10^{-5}$ according to the measured values. Mixed effects of density and thermal relaxation cause this deviation.

7. CONCLUSIONS

The German D1-Mission will provide adequate experimential conditions in micro-gravity environment for longterm c_V measurements. The HPT-calorimeter mechanically and functionally described in this paper is expected to furnish valuable data of the isochoric speciphic heat c_V that is free from gravitational influences. The experimental results will serve as important references for further theoretical investigations. Furthermore terrestrial experiments still have no access to the immediate vicinity around the critical point not even whith highly sophisticated electronic control systems. It will be the aim of HPT μ-g experiment program to intrude this region and supply data without the disturbing effects of density sedimentation.

9. REFERENCES

BAKER G.A.jr., NICKEL B.G., MEIRON P.I., (1976) : "Critical indices from perturbation analysis of the Callan-Symanzik equation", Phys. Re. B17, 1365

BUCKINGHAM M.J.,EDWARDS C., LIPA, J.A., (1973) : "A high precision scanning ratio calorimeter for use near phase transitions", Rev. Sci. Instrum. 44, No. 9, 1167-1172

CAMP W.J. et al., (1978) : "Series analysis of correction to scaling for the spin-pair correlations of the spin-s Ising Model: Confluent singularities, universality, and hyperscaling", Phys. Rev. B14, 3990-4001

HOHENBERG P.C., BARMATZ M. (1972) : "Gravity effects near the gas-liquid critical point", Phys. Rev. A6, No.1, 289-313

LANGE R., (1983) : Die Anomalie der isochoren Wärmekapazität im kritischen Gebiet von Schwefelhexafluorid", Dissertation Technische Universität München

LANGE R., STRAUB J., (1984): "Die isochore Wärmekapazität fluider Stoffe im kritischen Gebiet -Voruntersuchungen zu einem Spacelab-Experiment- ", Lehrstuhl A für Thermodynamik, Technische Universität München, Forschungsbericht BMFT-FB-W 84-034

STRAUB J., (1977) : "Kritische Phänomene in Fluiden", Habilitationsschrift, Technische Universität München

WÜRZ U., GRUBIC M., (1980) : "An adiabatic calorimeter of the scanning ratio type", J.Phys.E: Sci. Instrum. 13, 525-529