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Isochoric *pvT* Measurements of SF_6 in the Density Range 100 to 1200 $kg \cdot m^{-3}$ [1]

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The *pvT* properties of SF_6 were determined by an isochoric method. The pressure p and the temperature T were measured in the pressure range $1.5\ \mathrm{MPa} \leqslant p \leqslant 9.0\ \mathrm{MPa}$ and in the temperature range $293\ \mathrm{K} \leqslant T \leqslant 340\ \mathrm{K}$. The results are compared with data in the literature. The adsorption of SF_6 on glass and iron surfaces and its influence on the *pvT* measurements are also briefly discussed.

KEY WORDS: adsorption isotherm; compressibility factor; equation of state; isochoric measurement; SF_6.

1. INTRODUCTION

Sulfurhexafluoride (SF_6) is a chemically stable nonpolar compound which has been used increasingly by industry in the past years. Due to the symmetric properties of the molecule, SF_6 is also of increasing theoretical importance for the investigation of intermolecular forces.

The setting up of empirical equations of state is most useful for technical purposes. In order to meet the high accuracy requirements for reproducing the thermodynamic properties over wide temperature and pressure ranges, a large number of measured values affected by as low an uncertainty as possible is required. To allow the small uncertainty of 0.3×10^{-3} to be reached in the determination of the compressibility factor, a new apparatus has been designed and constructed. The apparatus and initial measurements with nitrogen have been described recently [1].

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The present paper reports the results obtained for SF_6 in the density range 100 to 1200 $kg \cdot m^{-3}$ and compares them with those published by Biswas et al. [2]. The type of empirical correlation equation used in this paper and proposed by Angus et al. [3] does not claim to be generally valid in other pvT regions; in the pressure, temperature, and density ranges investigated here it can, however, be applied for interpolation purposes within the scope of the uncertainties stated for the reproduction of the equation.

2. EXPERIMENTS AND THEIR EVALUATION

The pvT properties of SF_6 (purity 99.998%) were determined by a method of constant volume. Isochores were measured in the temperature range $293\ K \leqslant T \leqslant 340\ K$ and the pressure range $1.5\ MPa \leqslant p \leqslant 9\ MPa$.

Figure 1 shows a schematic diagram of the apparatus. A quantity of gas is filled into the thermostated measuring cell of constant volume. The pressures resulting at various temperatures are then measured. All points of measurement are located approximately on an isochore. The volume $V(T_R)$ of the measuring cell at the temperature $T_R = 298.15$ K was determined by weighing with water, with a relative uncertainty of 1×10^{-4}. The volume of the chamber of the differential pressure indicator (DPI) was determined

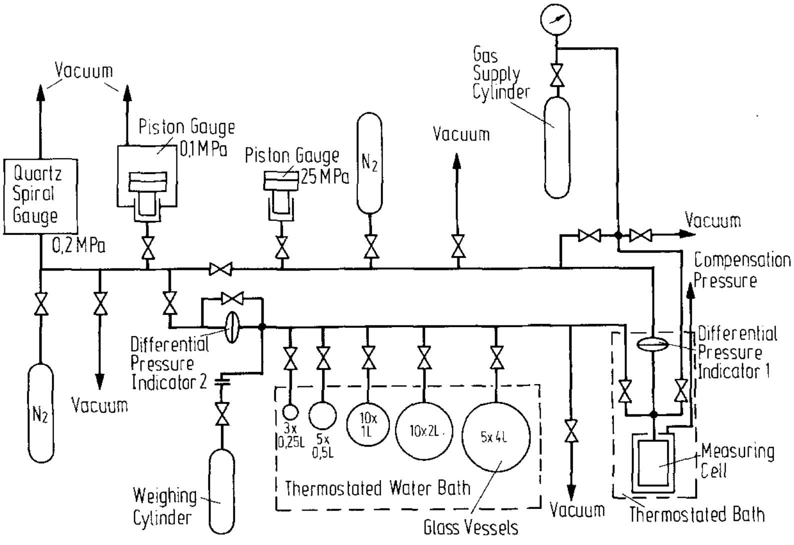

Fig. 1. Schematic diagram of the constant-volume apparatus.

with sufficient accuracy by gas volumetry. The volume $V(T)$ of the measuring cell at the temperature T is calculated from Eq. (1) to be

$$V(T) = V(T_R)[1 + \beta(T, T_R)(T - T_R)] \tag{1}$$

$\beta(T, T_R)$ is the mean cubic thermal expansion coefficient of the material used between T and T_R calculated from the mean linear thermal expansion coefficient experimentally determined at the PTB.

To reduce the pressure expansion to practically zero, the measuring cell is surrounded by a pressure vessel whose internal pressure is equal to that prevailing in the measuring cell. During the measurement, the pressure in the pressure measuring system is adjusted by means of the DPI so that it is equal to the pressure of the test fluid. The atmospheric pressure and pressures below 0.2 MPa are measured with a quartz spiral gauge (DDR 6000, Ruska Corp.). The relative uncertainty of measurement is 1×10^{-4}. A piston gauge (Desgranges & Huot) is used to measure gauge pressures of $0.2\ \mathrm{MPa} \leqslant p \leqslant 12\ \mathrm{MPa}$. In this case, the pressure-dependent relative accuracy amounts to about 5×10^{-5}.

For measuring temperatures, 25-Ω Pt resistance thermometers (Tinsley & Co.) are used which have been calibrated according to the specifications of the International Practical Temperature Scale of 1968 (IPTS-68). The electrical resistance of the thermometers is measured with an automatic resistance bridge (F17, Automatic Systems Laboratories). The uncertainty of the temperature measurement is 1 mK. The data are recorded and evaluated by a computer. Only the numbers of the weights on the piston gauge and the numbers of the glass vessels used to determine the mass are entered into the computer via the keyboard.

For determining the mass, the gas from the measuring cell is allowed to expand into evacuated glass vessels of known volume, to about 0.1 MPa at constant temperature (293 K). After thermal equilibrium has been reached, the temperature T and the pressure p inside the glass vessels are measured.

By applying the virial equation of state, which—for SF_6 at pressures $p < 0.1$ MPa—can be terminated after the second virial coefficient $B(T)$, the mass m of the gas can be determined by means of the following equation:

$$m\left[1 + B(T)\frac{m}{MV}\right] = \frac{pMV}{RT} \tag{2}$$

V is the volume of the glass vessels and supply tubes, p the pressure, M the molar mass of SF_6 ($M = 140.056\ \mathrm{g \cdot mol^{-1}}$), T the absolute temperature, R the gas constant ($8.314510\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), and $B(T)$ the second virial coefficient.

By five expansion runs in the glass vessels the second virial coefficient was determined to be $B(293.20\ \mathrm{K}) = (-282.7 \pm 2.3)\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. This value was used in all determinations of the mass. The relative uncertainty of the determination of the mass is estimated to be 2×10^{-4}.

3. INFLUENCE OF ADSORPTION

Figure 2 shows typical adsorption isotherms of the SF_6/iron powder system at $T = 303$ K and $T = 323$ K and for the SF_6/Duran glass powder system at $T = 293$ K. The adsorption isotherms were determined gravimetrically using a microbalance. The measuring principle and the apparatus have already been described in detail in the report on the investigation of the *pvT* properties of natural gas [4].

The influence of this adsorption can be estimated on the basis of the measurements of the adsorption of SF_6 on glass powder and iron powder. The glass vessels used in the apparatus have a geometric surface of $A \cong 2\ \mathrm{m}^2$. From Fig. 2 an adsorbed mass of $m(\mathrm{ads}) = 0.05\ \mathrm{mg} \cdot \mathrm{m}^{-2}$ can be read for the adsorption of SF_6 on Duran glass powder at $T = 293$ K and $p = 0.1$ MPa. The error of the mass due to adsorption on the glass vessels is $\Delta m/m = 1.25 \times 10^{-6}$ at its maximum.

A similar result is obtained for the adsorption of SF_6 on the geometric surface of the measuring cylinder used. If it is assumed that the adsorbability of SF_6 on iron powder at $T = 303$ K can be transferred to the material of the measuring cell used in the experiment (stainless steel), $\Delta m/m = 2.5 \times 10^{-6}$ is obtained for the error of the mass. A comparison with

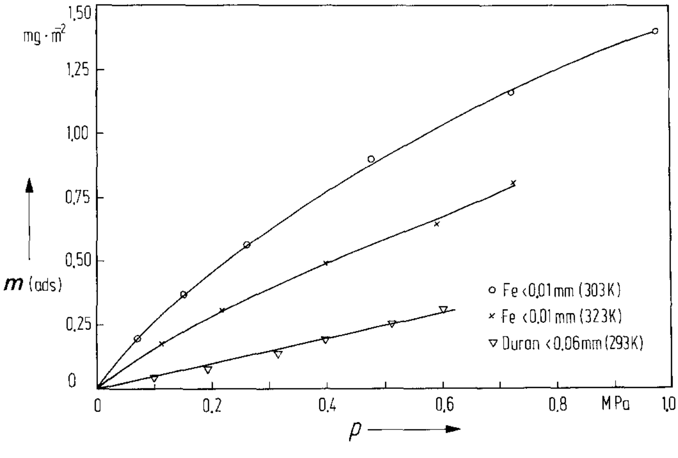

Fig. 2. Adsorption isotherms of SF_6 on glass and iron surfaces.

the relative uncertainty of the determination of the mass shows that the overall influence of the adsorption on the determination of the mass need not be corrected.

4. RESULTS

Figure 3 shows the isochores discussed in the present paper (circles) and those given in the report by Biswas et al. [2] (crosses).

Table I gives the original values obtained in the measurements of the pressure p, the temperature T, and the density ρ. The pressure values measured along the isochores can be expressed very well by a polynomial of the third degree in T. A polynomial represented by Eq. (3) was fitted to the measured data points by using a Gaussian least-squares fit.

$$\frac{p}{\mathrm{MPa}}=a_0+a_1\left(\frac{T}{\mathrm{K}}\right)+a_2\left(\frac{T}{\mathrm{K}}\right)^2+a_3\left(\frac{T}{\mathrm{K}}\right)^3 \tag{3}$$

The coefficients a_0, a_1, a_2, and a_3 are shown in Table II.

The uncertainty of the intermediate values calculable with these polynomials is estimated to be of the same order of magnitude as that of the measured values.

5. COMPARISON OF THE DATA WITH THE LITERATURE

In order to allow a better comparison of the pvT properties in the form of the compressibility factor $Z=(pM/\rho RT)$ measured within the

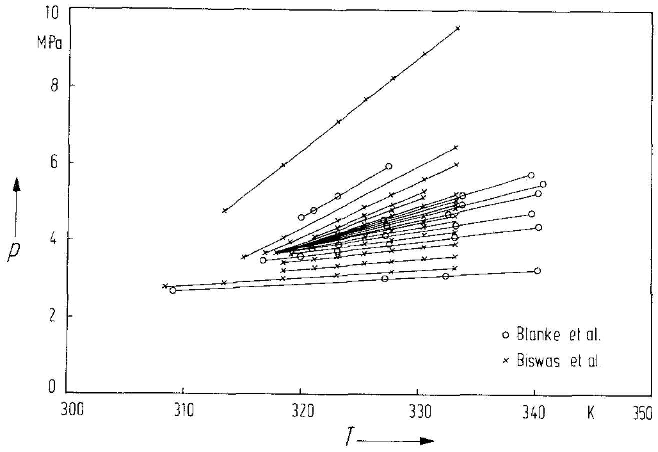

Fig. 3. Isochoric measurements of SF_6 from this work and those of Biswas et al. [2].

Table I. Experimental $p\rho T$ Data of SF_6 Along Isochores in the Density Range $100 \leqslant \rho \leqslant 1200\ kg \cdot m^{-3}$

Run No.	ρ ($kg \cdot m^{-3}$)	T (K)	p (MPa)
1	120.69	293.365	1.56489
	120.54	319.949	1.79703
	120.52	323.064	1.82415
	120.49	327.156	1.85918
2	154.53	293.327	1.85582
	154.48	299.509	1.93220
	154.40	310.123	2.05875
	154.33	318.740	2.15976
	154.25	330.190	2.29129
	154.17	340.022	2.40142
3	239.47	309.252	2.67373
	239.26	327.209	3.04130
	239.19	332.394	3.14450
	239.10	339.946	3.29241
4	404.24	316.825	3.49034
	404.18	319.913	3.61906
	404.16	323.067	3.74826
	404.12	327.514	3.92766
	403.77	333.077	4.14867
	404.03	340.003	4.41878
5	495.01	320.854	3.81825
	495.01	320.854	3.81821
	495.01	320.854	3.81802
	495.01	320.856	3.81826
	494.95	323.101	3.93886
	494.95	323.110	3.93888
	494.95	323.111	3.93882
	494.86	327.189	4.15399
	494.86	327.192	4.15403
	494.86	327.196	4.15390
	494.71	333.079	4.45823
	494.71	333.083	4.45825
	494.56	339.460	4.78254
	494.56	339.463	4.78258
	494.56	339.465	4.78250

Table I. (*Continued*)

Run No.	ρ (kg · m^{-3})	T (K)	p (MPa)
6	628.95	319.757	3.82541
	628.95	319.758	3.82546
	628.95	319.760	3.82546
	628.85	322.917	4.05294
	628.85	322.919	4.05292
	628.71	327.358	4.36575
	628.71	327.363	4.36547
	628.56	332.536	4.72605
	628.56	332.540	4.72596
	628.33	339.944	5.23864
	628.33	339.944	5.23810
	628.33	339.945	5.23791
7	709.18	319.744	3.83659
	709.18	319.751	3.83660
	709.14	320.895	3.92940
	709.14	320.896	3.92947
	709.07	322.911	4.09110
	709.07	322.911	4.09164
	709.07	322.915	4.09122
	708.97	327.348	4.44928
	708.70	333.657	4.95887
	708.47	340.298	5.49679
8	820.35	319.401	3.81607
	820.27	321.640	4.02346
	820.27	321.641	4.02357
	820.23	322.646	4.11988
	820.05	326.977	4.53756
	820.05	326.979	4.53767
	820.05	326.979	4.53774
	819.78	333.719	5.20184
	819.78	333.720	5.20193
	819.55	339.353	5.76510
	819.55	339.353	5.76489
	819.55	339.353	5.76510
9	1129.05	319.979	4.61506
	1128.95	321.021	4.80406
	1128.99	321.023	4.80400
	1128.88	323.027	5.16827
	1128.88	323.030	5.16828
	1128.64	327.340	5.96137

Table II. Coefficients a_k of the Interpolating Polynomials $p=\sum_{k=0}^{3} a_k T^k$ Fitting the Quasi-Isochores

Run No.	a_0	a_1	a_2	a_3
1	-2.38552700	$2.18202300 \times 10^{-2}$	$-4.09935000 \times 10^{-5}$	$4.26660400 \times 10^{-8}$
2	-4.92146548	$3.94284525 \times 10^{-2}$	$-7.46702719 \times 10^{-5}$	$6.48518338 \times 10^{-8}$
3	$-7.19527300 \times 10^{1}$	$4.43161500 \times 10^{-1}$	$-6.53169600 \times 10^{-4}$	0
4	$-5.32313423 \times 10^{1}$	$4.20134188 \times 10^{-1}$	$-1.08922562 \times 10^{-3}$	$1.03599846 \times 10^{-6}$
5	$-1.01715434 \times 10^{2}$	$8.30972892 \times 10^{-1}$	$-2.27221512 \times 10^{-3}$	$2.20492623 \times 10^{-6}$
6	$-2.03330085 \times 10^{2}$	1.72661027	$-4.94806867 \times 10^{-3}$	$4.92370825 \times 10^{-6}$
7	-7.90848176	$-4.19747713 \times 10^{-2}$	$3.55831591 \times 10^{-4}$	$-3.43008327 \times 10^{-7}$
8	2.39579136×10^{2}	-2.27647392	$7.03109016 \times 10^{-3}$	$-6.93421797 \times 10^{-6}$
9	$-1.20991839 \times 10^{3}$	1.10175499×10^{1}	$-3.38436357 \times 10^{-2}$	$3.52328362 \times 10^{-5}$

scope of this paper with those found by Biswas et al. [2], the following equation of state used by Angus et al. [3] for chlorine was fitted to both data sets:

$$Z = 1 + A\omega + B\omega^2 + C\omega^3 + D\omega^5 + E\omega^7 + F\omega^9 + H\omega^4 + K\omega^8 + M\omega^{10} + N\omega^{12} + Q\omega^{14} \qquad (4)$$

For the temperature dependence of the coefficients of Eq. (4), the following is valid:

$$\begin{aligned}
A &= P_1\tau^{5/4} + P_2\tau^4 + P_3\tau^{7/4} \\
B &= P_4\tau^{5/4} + P_5\tau^4 + P_6\tau \\
C &= P_7\tau^4 \\
D &= P_8\tau^2 + P_9\tau^4 \\
E &= P_{10}\tau^4 \\
F &= P_{11}\tau^3 \\
H &= P_{12}\tau^3 \exp(-\omega^2) \\
K &= P_{13}\tau^5 \exp(-\omega^2) \\
M &= P_{14}\tau^4 \exp(-\omega^2) \\
N &= P_{15}\tau^3 \exp(-\omega^2) \\
Q &= (P_{16}\tau^5 + P_{17}\tau^4 + P_{18}\tau^3) \exp(-\omega^2)
\end{aligned} \qquad (5)$$

with $\tau = T_c/T$ and $\omega = \rho/\rho_c$; $T_c = 318.7$ K and $\rho_c = 730\ \mathrm{kg \cdot m^{-3}}$ are the critical temperature and the critical density, respectively. The coefficients P_1 to P_{18} are listed in Table III.

The equation of state [Eq. (4)] was fitted to a total of 217 measured *pvT* data points by nonlinear regression with a mean standard deviation of $\bar{\sigma} = 1.03 \times 10^{-5}$.

Figures 4, 5, and 6 show the relative deviation of the compressibility factor $\Delta Z = [Z(\mathrm{cal}) - Z]/Z$ of the results of Biswas et al. [2] (crosses) and of this paper (circles) as a function of the density ρ, the temperature T, and the measured compressibility factor Z from the equation of state applied. With only a few exceptions, the deviations of the measured compressibility factors lie within a range of $\pm 2 \times 10^{-3}$. This is a good reproduction of the measured compressibility factors, in particular if it is borne in mind that the terms of the type of equation of state used have not been optimized.

Table III. Numerical Values of the Coefficients P_i of the Equation of State [Eq. (4)] with $T_c = 318.7$ K and $\rho_c = 730\ \mathrm{kg \cdot m^{-3}}$

Coefficient	Value
P_1	-1.7757415148
P_2	$-5.5617242296 \times 10^{-1}$
P_3	1.2603733632
P_4	-6.9830753422
P_5	$-3.6097514612 \times 10^{-1}$
P_6	6.9666074380
P_7	2.0790050287
P_8	$-1.0784934731 \times 10^{-1}$
P_9	$-7.0422979117 \times 10^{-1}$
P_{10}	1.0701925439
P_{11}	$-4.6416454924 \times 10^{-4}$
P_{12}	-1.6903517732
P_{13}	$3.9450238961 \times 10^{-2}$
P_{14}	$-1.7234780079 \times 10^{-1}$
P_{15}	$9.4574437674 \times 10^{-2}$
P_{16}	$-4.1501807747 \times 10^{-4}$
P_{17}	$-1.0251762688 \times 10^{-2}$
P_{18}	$-3.7889317095 \times 10^{-3}$

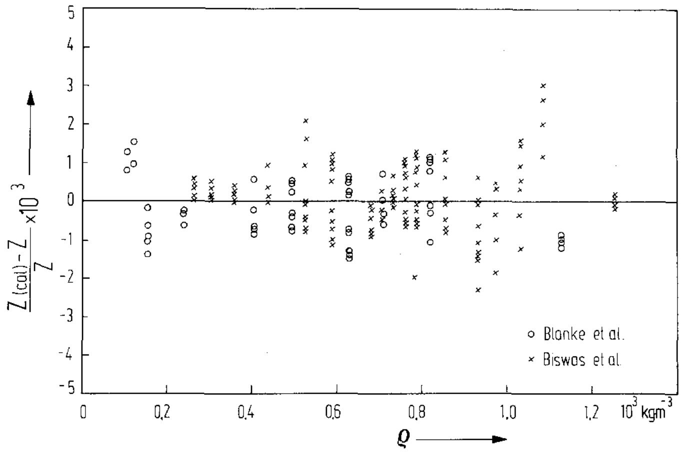

Fig. 4. Relative deviation of the compressibility factor from the equation of state as a function of the density.

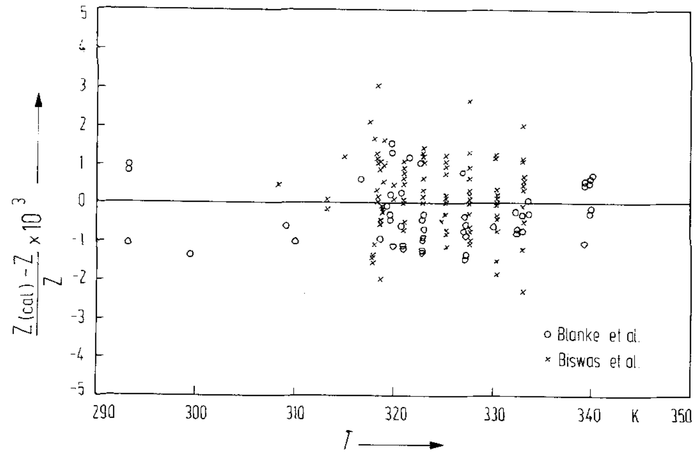

Fig. 5. Relative deviation of the compressibility factor from the equation of state as a function of the measured compressibility factor.

Measurements of the volumetric properties of SF_6 from 260 to 340 K at pressures to 2.5 MPa were published by Mollerup in 1985 [5]. Only four data points lie within the range of our measurements; they were not used for the fitting of the equation of state [Eq. (4)]. A comparison of the data in the range 285 to 340 K and densities in the range 122 to 163 $kg \cdot m^{-3}$ results in a mean relative deviation from the equation of state [Eq. (4)] of 6.8×10^{-4}, the greatest deviation being smaller than 1.4×10^{-3}.

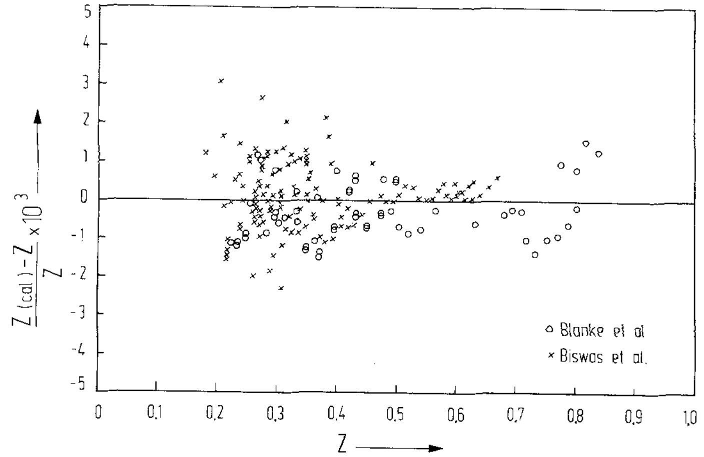

Fig. 6. Relative deviation of the compressibility factor from the equation of state as a function of the temperature.

In conclusion, it can be said that the *pvT* values measured within the framework of the experiments described here are in good agreement with data in the literature.

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