Compressibility of SF_6 along the critical isochore (on the value of the critical exponent γ)

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The compressibility of SF_6 along the critical isochore has been measured by a visual observation technique. Nineteen isotherms were recorded in the range $T-T_c=0.0027$–1.0293 °C. The measurement errors were $\pm 2\times 10^{-4}$ °C for the temperatures, $\pm 4\times 10^{-4}$ kgf/cm² for the pressures, and ±0.02% for the volumes. The experimental data are satisfactorily represented by the usual power law but with two values for the exponent: $\gamma=1.00$ near the critical temperature ($\tau<10^{-3}$), and $\gamma=1.16\pm 0.03$ farther from it ($\tau>10^{-3}$).

Near the critical point we have

$$(\partial P/\partial V)_T=A(T-T_\text{к})^\gamma \text{ at } V=V_\text{к}. \tag{1}$$

According to contemporary theories of the critical phenomena, the critical exponent γ is greater than unity (~1.20—1.30), whereas the classical theory gives $\gamma = 1.0$. There is a considerable amount of experimental data supporting the larger values for γ. As far as we are aware, however, in most cases γ was evaluated from data on light scattering or the density distribution in the gravitational field[1], and the degree of approximation to the critical point was no better than 0.002 (as measured by the ratio $(T - T_C)/T_C$). The only exception is the work of Balzarini[2]. Virtually no direct measurements of the compressibility along the critical isochore have been made. We are aware of three papers[3-5]; their results agree well, but the experimental accuracy and closeness of approach to the critical point are clearly inadequate by present day standards.

P-V-T measurements are simpler and more reliable than other methods of determining the compressibility, so a precise determination of $(\partial P/\partial V)_T$ along the critical isochore, in which the dependence of the pressure on the volume along the isotherm would be measured, is of interest. A precision technique has been developed for this purpose; it enables one to improve the accuracy of the measurements by about an order of magnitude as compared with the measurements to be found in the literature. The closeness of approach to the critical point was also improved by about an order magnitude.

Our measurements were made by visual observation, using apparatus described in detail in[6]. The principal piece of apparatus was a horizontal piezometer with a continuously variable volume and a vertical dimension of only 8 mm (Fig. 1). The volume of the piezometer could be varied continuously by ±10% of the total with an error of ±0.01%. The investigated material was measured out by weight with an error of ±0.005%. The over-all error in the volume measurements was ±0.02%. The piezometer was mounted in a 70 liter water thermostat whose temperature was measured with a platinum resistance thermometer. The temperature could be reliably measured and held constant within $\pm 2\times 10^{-4}$°C in the intrinsic scale of the thermometer. We did not observe any temperature gradients along the piezometer; in any case, the temperature drop along the piezometer did not exceed 1×10^{-4}°C.

The pressure was measured with a piston-type dead weight tester selected from the group of USSR standards. The over-all error in measuring the pressure amounted to $\pm 4\times 10^{-4}$ kgf/cm² (±0.001%).

For our study we chose sulfur hexafluoride (SF_6). The material was purified by multiple distillation on a high-pressure fractionating column. The final distillation was carried through on a specially made "fine purifying" column. The method used to remove air from the SF_6, which was developed by the authors, made it possible to reduce the air contamination to 1×10^{-7}%, or lower.

The purity of the SF_6 was tested as follows. The piezometer was charged with SF_6 until there remained only a small bubble of the gaseous phase. The system was then thermostated and the pressure was measured at a fixed temperature. Then SF_6 was removed from the piezometer until there remained only a small quantity of the liquid phase, and the pressure was again measured at the same temperature. In such tests we were unable to detect any pressure change beyond the experimental errors at a temperature of 35.2542% C with the volume ranging[1] from 120 to 490 cm³/mole. These results yield 99.9995% as a rough estimate of the purity of the SF_6.

The purity of the SF_6 was checked as described above after each run. Experience with ultrapure substances has shown that it is frequently more difficult to keep the material pure during storage and while transferring it to the apparatus for study than to purify it in the first place. We therefore developed the following technique for storing and measuring out the SF_6: The SF_6 was stored in a stainless steel vessel, which had been polished on the inside, carefully, washed, and outgassed by heating while pumping down to 10^{-6} mm Hg. All the internal parts of the apparatus (the piezometer, valves, and mercury presses) were washed with pure SF_6 and then pumped down.

We used doubly distilled mercury. Before being put into the apparatus, the mercury was treated with SF_6 and then pumped down while being heated. Especial attention was given to washing and degassing the Teflon gaskets. According to information that we have, Teflon can selectively absorb certain gasses (CO_2 and others), and this may lead to subsequent contamination of the investigated substance.

Many methods for determining the critical constants are now known. However, we undertook an experimental comparison of all these methods, which showed that the visual method is the most accurate and reliable. On

TABLE I. Critical constants of SF_6

T_c, °C	P_c, kgf/cm²	V_c, cm³/mole	Source
$45.5730 \pm 2 \cdot 10^{-4}$	$38.3280 \pm 4 \cdot 10^{-4}$	198.06 ± 0.05	The present work
$45.547 \pm 5 \cdot 10^{-3}$	$38.337 \pm 3 \cdot 10^{-3}$	200	[9]
$45.555 \pm 5 \cdot 10^{-3}$	—	194.4	[10]
$45.58 \pm 1 \cdot 10^{-2}$	38.32	199	[11]
$45.560 \pm 5 \cdot 10^{-3}$	$38.328 \pm 5 \cdot 10^{-3}$	198.0 ± 0.4	[12]

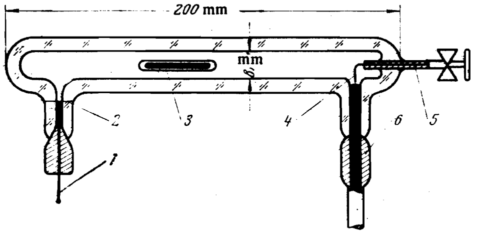

FIG. 1. Piezometer: 1—capillary for introducing mercury, 2—mark indicating the mercury reference level, 3—agitator, 4—electrical lead to the pressure measurement line, 5—capillary for introducing the investigated material, 6—nipple on the pressure measurement line.

analyzing the results obtained in the present study one can easily show that any other method for determining P_c, T_c, and V_c leads to errors an order of magnitude larger, despite the fairly high accuracy of the raw data (Table 1). The reason is that all these methods are based on comparing the values of derivatives ($(\partial P/\partial V)_T$, $(\partial P/\partial T)_V$, etc.) or even their differences. The technique for the visual determination of the critical constants has been described in detail in[7,8], so we shall not dwell on it here.

The critical constants of SF_6 as determined by various investigators are listed in Table I.

The measurements were made as follows. An appropriate amount of SF_6 was introduced into the piezometer, the amount being chosen so that the critical density would be reached at about the middle of the range of variation of the piezometer volume (±10% of the total volume). The compressibility was measured by recording isotherms. To do this the desired temperature was established and the pressure was varied at different volumes. The piezometer volume was varied by introducing mercury through capillary 1 (Fig. 1).

Particular attention was given to the establishment of equilibrium in the system. As criteria for equilibrium we used the constancy of the pressure and the absence of hysteresis on approaching equilibrium from opposite sides (as regards both temperature and volume). Actually, the rate of establishment of equilibrium always corresponded to the thermal lag of the system. When the temperature was changed rapidly by $(1-2) \times 10^{-3}$°C equilibrium would be established within two or three minutes. The shape of the agitator and the manner of using it were chosen with care. This was necessary because the heat introduced into the system on operating the agitator (because of friction with the working substance, with the walls, etc.) could not be calculated and might significantly affect the results of the measurements[7]. We moved the agitator along the piezometer about ten times per minute. The small vertical dimension of the piezometer and the intense mixing enabled us to avoid the gravity effect.

To improve the reliability of the data we measured the pressure on each isotherm both on increasing the volume and on decreasing it. Figure 2 shows one of the resulting isotherms ($T - T_c = 0.0124$°C). The absence of hysteresis proves that the data refer to the equilibrium state.

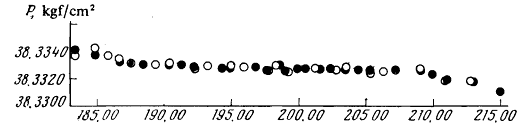

FIG. 2. Isotherm for SF_6 ($T - T_c = 0.0124$°C) in the p-V plane: the open (black) circles mark points recored on increasing (decreasing) the volume. The experimental errors do not exceed the size of the circles.

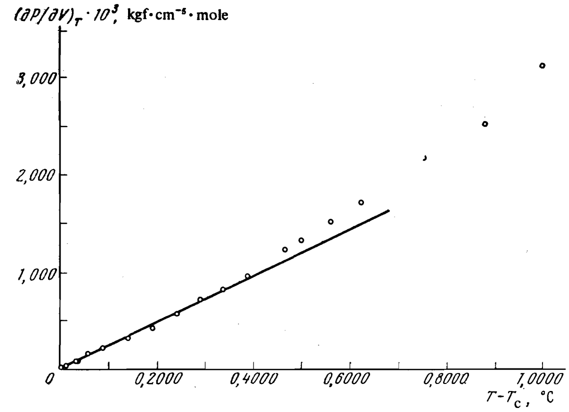

FIG. 3. $(\partial P/\partial V)_T$ vs $T - T_c$ on the critical isochore; the line was drawn for $\gamma = 1$.

TABLE II. $(\partial P/\partial V)_T$ at $V = V_c$

$(\partial P/\partial V)_T \cdot 10^3$, kgf·cm⁻⁵·mole	$T-T_c$, °C	$\pm(\delta P/\Delta P)_T$, %	No. of points on the isotherm in the interval $V_c \pm 8\%$	$(\partial P/\partial V)_T \cdot 10^3$, kgf·cm⁻⁵·mole	$T-T_c$, °C	$\pm(\delta P/\Delta P)_T$, %	No. of points on the isotherm in the interval $V_c \pm 8\%$
0.008 *	0.0027	100	50	0,820	0.3363	2	30
0,029	0.0124	30	50	0.960	0.3877	2	30
0.076	0,0338	8	50	1.230	0.4657	1	20
0.081	0.0366	8	50	1.320	0,5007	1	20
0.156	0.0583	4	50	1.510	0.5595	1	15
0.214	0,0892	3	40	1.710	0.6237	1	15
0,313	0.1398	2	40	2.170	0,7527	1	15
0,416	0,1913	2	40	2,490	0.8808	1	15
0,565	0.2407	3	30	3.110	1.0293	1	15
0.707	0.2873	1	30				

*This point was not used in the subsequent calculations.

All the measurements were made (and the critical constants determined) with one charge of SF_6. We determined the pressure-volume relationship on 19 isotherms in the range $T - T_c = 0.0027-1.0293$°C covering the volume interval 180—220 cm³/mole.

The absolute value of $(\partial P/\partial V)_T$ decreases on approaching the critical point, so we made special efforts to obtain accurate data on the isotherms close to the critical one. Specifically, we recorded 50 points in the interval $V_c \pm 8\%$ on each of the five isotherms closest to T_c. Fewer points were recorded on the isotherms farther from T_c, and only 15 points on the farthest ones. Thus, the (absolute) error in calculating $(\partial P/\partial V)_T$ was least on the isotherms closest to T_c; it amounted to $\pm 8 \times 10^{-6}$ kgf·cm⁻⁵·mole.

We evaluated $(\partial P/\partial V)_T$ (Table II and Fig. 3) and $B = (\partial P/\partial V)_T \approx (\partial^2 P/\partial V \partial T)$ (Fig. 4) from the resulting data, using both graphical methods and a computer. The calculations were facilitated by the fact that the isotherms in the P-V plane had definite rectilinear sections in the vicinity of V_c. As T receded from T_c, the length of this section decreased from 10% of V_c to 2% of it.

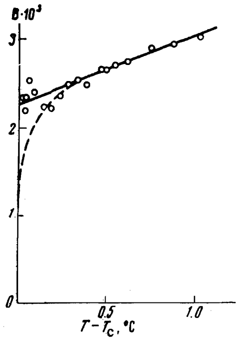

FIG. 4

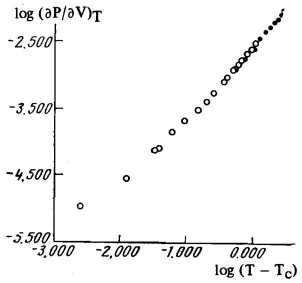

FIG. 5

FIG. 4. $B = (\partial P/\partial V)_T/\Delta T$ vs $T - T_c$. The circles represent experimental data, the heavy line is a linear approximation to the experimental data, and the dashed curve represents the equation $B \cdot 10^3 = -2.97 \Delta T^{0.16}$.

FIG. 5. Log $(\partial P/\partial V)_T$ vs log $(T - T_c)$ on the critical isochore; the open circles represent data from the present work, and the black circles, data from [3].

We also plotted the results as $\log(\partial P/\partial V)_T$ vs $\log(T - T_c)$ (Fig. 5).

The data in the interval $T - T_c = 0.35$–1.03°C can be described by Eq. (1) with $\gamma = 1.16$. However, this value of γ cannot be used for temperatures arbitrarily close to T_c. For small ΔT (< 0.4°C) the relationship is linear, as is evident from Fig. 3.

A least squares evaluation of γ shows that γ approaches unity as $T - T_c$ decreases toward zero:

ΔT, K:	1.03	0.62	0.46	0.34	0.24	0.14
$\tau \cdot 10^3 = (\Delta T/T_c) \cdot 10^3$:	3.23	1.95	1.44	1.06	0.75	0.44
No. of points :	18	15	12	10	8	6
γ:	1.05	1.04	1.02	1.01	0.99 *	1.01 *
$\sigma \cdot 10^5$:	9.07	4.7	3.38	2.01	1.50	1.34

(the asterisks mark quantities for which the correlation coefficient is 0.998). The same thing is also evident from Fig. 5.

The approach of γ to unity is also shown very clearly in Fig. 4. No decrease in B is observed at $\tau \leq 10^{-3}$, whereas such a decrease would necessarily occur if γ had any value other than unity. The quantity B remains finite as $\Delta T \to 0$; this means that $\gamma = 1$ near T_c.

From the point of view adopted above, the larger values of γ at relatively high temperatures arise simply because one is attempting to approximate the expansion $(\partial P/\partial V)_T = A\Delta T + B\Delta T^2 + \ldots$ by a power law. This approximation is not very accurate when points with small ΔT values ($\tau < 10^{-3}$) are included, as is shown by the increase in the standard deviation σ with increasing ΔT.

Our result evidently cannot be attributed to the gravity effect, since first, the pressure drop over the 8 mm height of the piezometer is only 5.6×10^{-4} kgf/cm², which hardly exceeds the experimental error in the pressure measurements (4×10^{-4} kgf/cm²), and second, the material was agitated, and this further reduces the gravity effect (although by an amount that unfortunately cannot be calculated).

Thus, precision measurements of the compressibility of SF_6 on the critical isochore have shown that

$$(\partial P/\partial V)_T = B(T - T_c)^{1.00} \tag{2}$$

and $(\partial P/\partial V)_T/\Delta T = \text{const} \neq 0$ for $\tau < 1 \times 10^{-3}$; only for $\tau > 1 \times 10^{-3}$ do we have

$$(\partial P/\partial V)_T = B(T - T_c)^{1.16 \pm 0.03}. \tag{3}$$

Our result that $\gamma = 1$ should probably not be regarded as surprising. Although the theory of similitude is fairly general, theoretical estimates of γ have been made[13] only on the basis of lattice models, which apparently are not valid for ordinary liquids near the critical point.

In concluding, we wish to thank I. R. Krichevskiĭ for help and advice in discussing the results, and V. I. Arakcheev for assistance with the computer calculations.

[1)] The maximum range of variation of the volume during the experiments was about five times smaller.

[1] Eugene H. Stanly, Introduction to Phase Transitions and Critical Phenomena, Oxford, 1971 (Russ. Transl., "Mir", 1973).

[2] D. A. Balzarini, Canad. J. Phys. 50, 2194 (1972).

[3] L. A. Makarevich, Zh. Fiz. Khim. 43, 2621 (1969).

[4] V. Jansoon, H. Gielen, and J. Baelpaep, Physica 46, 213 (1970).

[5] M. A. Weinberger and W. G. Schneider, Can. J. Chem. 30, 422 (1952).

[6] L. A. Makarevich and O. N. Sokolova, Zh. Fiz. Khim. 46, 1348 (1972).

[7] L. A. Makarevich, E. S. Sokolova, and G. A. Sorina, Zh. Fiz. Khim. 42, 1 (1968).

[8] L. A. Makarevich and O. N. Sokolova, Zh. Fiz. Khim. 47, 763 (1973).

[9] K. E. MacCormak and W. G. Schneider, Can. J. Chem. 29, 699 (1951).

[10] D. Atack and W. G. Schneider, J. Phys. Coll. Chem. 55, 532 (1951).

[11] H. P. Glegg, J. S. Rowlinson, and J. R. Sutton, Trans. Faraday Soc. 51, 1327 (1955).

[12] L. A. Makarevich, E. S. Sokolova, and G. A. Sorina, Zh. Fiz. Khim. 41, 2273 (1967).

[13] V. L. Pokrovskiĭ, Usp. Fiz. Nauk. 94, 127 (1968) [Sov. Phys.-Usp. 11, 66 (1968)].

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