Dielectric constant of ^{3}He near the liquid-vapor critical point

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High-resolution measurements of the static dielectric constant ϵ along the critical isochore are reported for ^{3}He in the region of the critical point. The experiments were conducted at a frequency of 1000 Hz and the purpose was to observe a divergence of $(\partial\epsilon/\partial T)_{\rho_c}$ as T_c is approached from above. No evidence for a critical anomaly was found, the estimated upper bound for its integrated value being $\delta\epsilon \sim 4\times10^{-8}$ which is consistent with the theoretical estimations. Hence, the recently reported enhancement in $\delta\epsilon$ for SF_6 over that predicted by theory is not observed in ^{3}He. In the Appendix, some experimental questions arising in such constant-density experiments are discussed.

I. INTRODUCTION

In this work we present high-resolution measurements of the static dielectric constant ϵ of ^{3}He near the liquid-gas critical point. These measurements were made to test the validity of recent theories which predict deviations from the behavior given by the Clausius-Mossotti equation,

$$(\epsilon-1)/(\epsilon+2)=\tfrac{4}{3}\pi\rho\theta_0 \ , \tag{1}$$

where ρ is the number density and θ_0 the polarizability of an isolated molecule. According to this equation, ϵ should be constant along a path of constant density.

The fundamental assumption behind the Clausius-Mossotti equation is that the polarizability of a molecule in the fluid is unchanged by the neighboring molecules. Far from the critical point, the fluctuations in the thermodynamic variables (for example, the density) are small and uncorrelated, thus the effect of neighboring molecules averages out and the Clausius-Mossotti equation can be expected to work quite well. However, in the critical region fluctuations become larger and the correlation between molecules increases. When these effects are included in the derivation, nontrivial correction terms appear.

The expected changes in the behavior of the dielectric constant in the critical region have been studied in recent years, beginning with Larsen, Mountain, and Zwanzig[1] and continued recently with the theories of Mistura,[2] Stell and Hoye,[3] and Bedeaux and Mazur.[4]

All of these more recent theories predict that the dielectric constant at the critical point is finite, but the slope $(\partial\epsilon/\partial t)_{\rho_c}$ diverges as a power law with some exponent x,

$$\left(\frac{\partial\epsilon}{\partial t}\right)_{\rho_c}\approx\left(\frac{\partial\epsilon}{\partial t}\right)_{\rm reg}+At^{-x} \ , \tag{2}$$

where $t=(T-T_c)/T_c$ and where $(\partial\epsilon/\partial t)_{\rm reg}$ expresses a regular part.

The theories by Mistura[2] and by Stell and Hoye[3] relate the divergence of $(\partial\epsilon/\partial t)_{\rho_c}$ to the specific-heat divergence, characterized by an exponent α, and thus predict $x\cong0.1$. The Bedeaux and Mazur theory relates ϵ to the correlation length $\xi=\xi_0 t^{-\nu}$ and gives $x\approx0.31$. Quantitative predictions by Stell[5] specifically for ^{3}He, and by Bedeaux and Mazur[4] indicate that the anomalous change in ϵ of fluids is small. It should nevertheless be resolvable in most fluids, but only marginally so in ^{3}He. However, an experimental study of sulfur hexafluoride (SF_6) along the critical isochore by Hocken, Horowitz, and Greer[6] revealed a very large anomalous change $\delta\epsilon$, more than ten times the size predicted by Bedeaux and Mazur. These authors also found the behavior of the slope $(\partial\epsilon/\partial t)_{\rho_c}$ was more complicated than that of a simple power-law divergence predicted by the theories. The discrepancies between the SF_6 result and the theory led us to make dielectric-constant measurements in ^{3}He; for a similar enhancement of $\delta\epsilon$ in ^{3}He the singular behavior would be observable with our capacitive techniques.

II. THEORY

The three recent theories mentioned are quite different in their approaches, but give the same qualitative behavior: a finite dielectric constant at the critical point and a divergent slope $(\partial\epsilon/\partial t)_{\rho_c}$. Mistura[2] uses the smoothness postulate to relate the singular part of the dielectric constant to the singular part of the internal energy, and shows that qualitatively $(\partial\epsilon/\partial t)_{\rho_c}$ should have a divergence like C_v, the

specific heat. This theory makes no quantitative predictions.

The theory of Stell and Hoye[3] starts with the expansion of the Clausius-Mossotti function

$$F_{CM}=[(\epsilon-1)/(\epsilon+2)](1/\rho)=\tfrac{4}{3}\pi\theta_0(1+S) \quad , \quad (3)$$

where S is expanded in powers of the polarizability. The authors show that the lowest-order term in the expansion is closely related to the internal energy and that if higher orders are neglected, it is reasonable to expect that the dielectric constant will have a singular part analogous to that of the internal energy.

Further work by Stell[5] specifically on ^{3}He produced an order of magnitude estimate for relating $(\partial\epsilon/\partial t)_{\rho_c}$ to the configurational specific heat

$$C_{\text{conf}}=(C_v/k_B-\tfrac{3}{2})k_B \quad .$$

The work of Kerr and Sherman[7] on the polarizability of ^{3}He showed that the dependence of the polarizability on the density was very nearly linear. Using this fact to justify omitting terms of higher order than linear in the density, Stell derived the quantitative relation between the slope dS/dT and C_{conf} on the basis of their similar functional form in terms of the radial molecular distribution function $g(r)$. Using numerical values of certain molecular interaction and polarizability parameters, he obtains an order-of-magnitude estimate

$$\frac{dS}{dT}\simeq\frac{-2\times10^{-4}\,C_{\text{conf}}}{k_B} \quad . \quad (4)$$

Finally, using the C_v data of Brown and Meyer,[8] we obtain a curve which is presented in Fig. 3, Sec. IV. Because $C_v\propto t^{-\alpha}$, and C_v/k_B and $\frac{3}{2}$ are comparable over a large portion of the temperature range of interest, C_{conf} reaches its asymptotic divergence ($\propto t^{-\alpha}$) only extremely close to T_c. The Stell and Hoye[3] theory does not predict a "universal" behavior for fluids, namely, the approximations which are expected to work for helium may not necessarily be adequate to describe a more complex fluid such as SF_6.

The theory of Bedeaux and Mazur[4] does not employ an expansion of the Clausius-Mossotti function, but develops an expression for the dielectric tensor in terms of the fluctuations of the hydrodynamic functions. From this approach the authors derive a closed form for the dielectric constant involving the density-density correlation function. Their result using the Ornstein-Zernike correlation function is

$$\epsilon_{\text{sing}}=-(1/54\pi)[(\epsilon+2)(\epsilon-1)^3/\epsilon]k_BTK_T\xi^{-3} \quad , \quad (5)$$

where $K_T=\Gamma t^{-\gamma}$ is the compressibility along the critical isochore and k_B is the Boltzmann constant. Making use of experimental values for ^{3}He,[9,10] with $\gamma\simeq1.17$ and $\nu\simeq0.62$, we obtain

$$\left(\frac{\partial\epsilon}{\partial t}\right)_{\rho_c}\approx-1.3\times10^{-6}t^{-0.31} \quad , \quad (6)$$

a result different from that obtained via Eq. (4) and which is also shown in Fig. 3. A review of the theories and a more detailed discussion of their applicability to SF_6 is given by Hocken, Horowitz, and Greer.[6]

Because of the finite experimental resolution in ϵ and in T, it turns out that the singular behavior of $(\partial\epsilon/\partial t)_{\rho_c}$ as predicted by theory will be resolvable best for $t<3\times10^{-3}$ above T_c. As the critical temperature is approached closer than about $t=10^{-4}$ the same difficulties appear as in measurements of C_v. Also, gravity effects can be expected to become important.

III. EXPERIMENTAL

Briefly, the experiment consists in measuring the dielectric constant along the critical isochore at a frequency of 1 000 Hz using a highly stable ratio-transformer capacitance bridge. At each measurement the temperature is stabilized within about 1 μK, the resolution is $\delta\epsilon/\epsilon\approx1\times10^{-8}$ and the range extends over $-0.1<t<0.1$. We will not discuss the region below T_c, where the capacitor samples the dielectric constant of two phases having different densities. We now describe in some detail the individual components.

A. Temperature measurement

The cryostat used in this experiment was designed specifically for use near the ^{3}He critical point and was capable of maintaining sample cell temperatures between 3 and 4 K with 1 μK control for long periods. The germanium resistance thermometer was calibrated against the T_{58}-^{4}He temperature scale, and we estimate that including systematic errors, our temperature scale is within 0.5 mK of T_{58}.

B. Sample cell

In the cell used, shown schematically in Fig. 1, the top and bottom pieces were 0.75 in. thick with a 1.2-in.-diam bolt circle. The height to diameter ratio was made large to reduce the pressure response to simple static compression. A 0.002-in.-thick layer of 2850FT Stycast epoxy was used to hold the plate in place while electrically insulating it from the grounded shell. For the temperature range T_c to (T_c + 10 mK), the pressure distortion effect caused a change in the capacitance $\delta C/C\approx-4\times10^{-7}$ as P increased at constant volume. Because $(\partial P/\partial T)_{\rho_c}\approx$ constant over this range[10] this change was linear in T and was easily calibrated and corrected for in the data analysis.

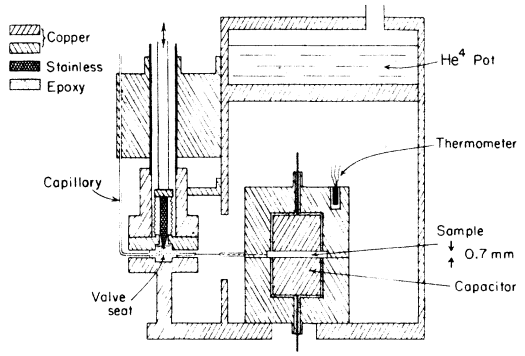

FIG. 1. Sample cell and valve. (a) German silver valve seat with 0.0025-in. hole for stainless-steel needle; (b) capillary above valve is 0.010-in.-i.d. stainless-steel tube, heat sunk to the pot; (c) valve stem is 0.010-in. wall thickness stainless-steel tube, heat sunk to the main ^{4}He bath above the ^{4}He pot; (d) capillary between valve and cell is 0.004-in.-i.d. stainless-steel tube.

The fill capillary consisted of a 0.008-in.-i.d. stainless-steel capillary from room temperature to the ^{4}He bath and to the pot, where it was heat sunk, and finally to the low-temperature valve. The thermal links between the valve and the bath were heat sunk to the pot to reduce any temperature gradients between the valve and the cell. The only remaining heat leak was down the inner valve stem which was heat sunk at the main ^{4}He bath temperature. With the bath at 4.2 K, this heat source was calculated to be less than 30 μW. The capillary from the valve to the sample cell was 0.004-in.-i.d. stainless steel, and the valve seat and capillary contained less than 0.4% of the total sample.

C. Capacitance bridge

Two arms of the bridge are provided by a ratio transformer, and the other two arms are the sample cell and standard capacitor. Details of the system are presented elsewhere[11] and will not be repeated here.

The capicitance bridge was run at 1 kHz and measured directly the ratio

$$R_C = C_{\text{sample}}/(C_{\text{sample}} + C_{\text{standard}}) \quad . \tag{7}$$

The step sizes of the different ratio-transformer steps were checked and found to be linear to at least the resolution of the bridge, about 2×10^{-9}, which corresponds to $\delta\epsilon \approx 1 \times 10^{-8}$ resolution in ϵ. The long-time bridge stability was to within the resolution and the data taken were very reproducible from day to day. Small shifts in the ratio occurred due to mechanical shock when the pot was filled before the experiment, but they were usually smaller than 1×10^{-7}.

D. Procedure

The ^{3}He sample with an isotopic purity of 99.99% was introduced into the cell at 3.5 K, in the one-phase region, and the density was checked two ways. The first method was to record the change in the capacitance. When corrected for the pressure effect (which was less than 0.3% of the total change $\delta C/C$ when ^{3}He was introduced), the capacitance change gave the density directly using the Clausius-Mossotti equation. Even if there was a large critical anomaly in ϵ, we felt that 3.5 K was far enough away from T_c to give an accurate density measurement. The polarizability used was

$$\Theta_0 = 0.1231 \text{ cm}^3/\text{mole}$$

from Ref. 7 and the critical density[9] was

$$\rho_c = 0.0137 \text{ mole/cm}^3 \quad .$$

The measured dielectric constant was then $\epsilon = 1.02145$.

The second method, used as a check on the first, was to interpolate the Behringer, Doiron, and Meyer[9] PVT data for ^{3}He to derive a pressure versus density diagram at the filling temperature. The densities measured by both methods were found to be within 0.2% of each other.

Both warming and cooling runs were made, and no hysteresis was found in the data. Some data points were taken at large temperature intervals away from the critical point, mostly to check the pressure effect, and each run included one particular temperature to check for day to day shifts in the capacitance ratio. The pressure distortion effect was found to be small, linear in the pressure, and consistent throughout the data taking.

The critical temperature was observable from two effects. As the critical temperature was crossed, there was a large change in the equilibrium times. In the one-phase region, equilibrium times were small, less than 5 min, while in the two-phase region the equilibrium times were over 20 min. Also, at the critical temperature there was a noticeable change in the behavior of the measured $(\partial\epsilon/\partial t)_\rho$, which was found to pass through a sharp peak. This observation was in fact an instrumental effect caused by a small constant temperature gradient between valve and cell, as will be discussed in the Appendix. By lowering the temperature of the main ^{4}He bath, thus reducing the heat leak and thermal gradient, we found we could minimize the change in ϵ without affecting the temperature of the peak, which was identified with T_c. We found $T_c = 3.3092$ K in good agreement with previous determinations.[8,9]

IV. RESULTS

The data in Fig. 2 were taken with the helium-bath temperature reduced to 3.5 K. No change in the dielectric constant occurred until the temperature reached 2 mK above T_c. Particularly in the range from 1 to 10 mK above T_c, where the predicted anomaly would be most visible, there is less than 1×10^{-7} change in ϵ, and most of that can be shown to be a remnant of the instrumental effect discussed in the Appendix. Thus, we have found no evidence of an anomaly substantially larger than our experimental scatter. Based on estimations of the instrumental effect, we would therefore place an upper limit of about 4×10^{-8} on the true dielectric constant anomaly.

To put an upper bound on the slope, since we saw nothing we could not account for, we can only state our resolution. In Fig. 3, we show a conservative upper bound for our measurements. The dashed line represents the slopes which would produce a dielectric constant change as large as our resolution for the temperature steps used in the experiments. The slopes in the shaded region below the dashed line are considered unresolvable in our experiment. Figure 3 also shows the SF_6 data and the predictions for ^{3}He and SF_6 by Stell[5] and by Bedeaux and Mazur,[4] respectively. For ^{3}He the order-of-magnitude estimates from theory are consistent with our findings. An integration of Stell's prediction[5] gives $\delta\epsilon \approx 2 \times 10^{-8}$ and a similar result for Bedeaux and Mazur.[4]

Both current theories[3,4] predict a very different behavior for SF_6 than for ^{3}He, and it is likely that SF_6 will have a much larger anomaly than ^{3}He, as for example the Bedeaux and Mazur[4] theory predicts. Thus, the existence of a large anomaly in SF_6 is not inconsistent with our results. However, as we discuss in the Appendix, there is a very great similarity between the SF_6 data of Hocken *et al.*[6] and the instrumental effect which we described earlier. This suggests that the same type of behavior might have occurred in their experiment, but until the experiment is carried out again with this problem in mind we cannot really judge whether the similarity is meaningful or merely a strange coincidence. If the SF_6 anomaly is confirmed it would be then most interesting to study the behavior of some gases which might have intermediate behaviors, such as neon, argon, and xenon. Such results would be most helpful in resolving the theoretical problems which now exist.

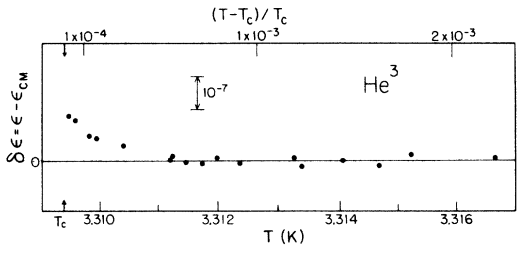

FIG. 2. Change $\delta\epsilon$ vs temperature for a bath temperature of 3.5 K. $\epsilon = 1.02145$.

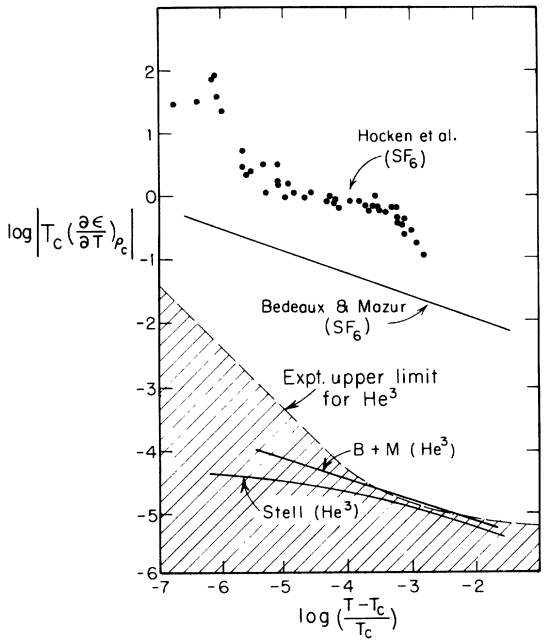

FIG. 3. Comparison of the SF_6 data, theoretical predictions, and the limit of resolution of this experiment.

V. CONCLUSION

We have measured the dielectric constant of pure ^{3}He along the critical isochore and have found no evidence of an anomaly in the critical region. After correcting the data for the small residual interaction between the gas in the valve and the sample cell due to small heat leaks, there was no resolvable change in the dielectric constant. Considering the scatter in the data and the resolution of our bridge, we would place a very conservative upper limit on such an anomaly in the dielectric constant at four parts in 10^8.

From a practical point of view it appears then that the Clausius-Mossotti relation represents extremely well the ρ and ϵ data for ^{3}He even in the critical region, when allowance is made for weak nonsingular dependence of the polarizability on the density.[7]

The stimulation to this research was provided by the large discrepancy between theory and experiment for SF_6 near the critical point. However for ^{3}He the experiment does not confirm the enhancement of $\delta\epsilon$ over that predicted by theory.

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APPENDIX

Since our study of ϵ for ^{3}He has produced a quite different result than that obtained[6] for SF_6, and the predicted anomaly for ^{3}He is small,[5] we shall describe in some detail[12] the instrumental effect in ϵ to which we alluded earlier. This effect arises from the density gradient between the valve (containing 0.4% of the sample) and the sample cell caused by a temperature gradient ΔT and a pressure gradient ΔP. A heat leak into the valve will be responsible for a

$$\Delta T = T_{\text{valve}} - T_{\text{cell}} ,$$

while a height difference between the space immediately below the valve and the cell will give

$$\Delta P = P_{\text{valve}} - P_{\text{cell}} .$$

We then have

$$\Delta\rho/\rho = (\rho_{\text{valve}} - \rho_{\text{cell}})/\rho = -\alpha_P \Delta T - K_T \Delta P , \quad \text{(A1)}$$

where α_P and K_T are, respectively, the thermal expansion and compressibility coefficients. Including their temperature dependence we have

$$\Delta\rho/\rho \simeq (-A\,\Delta T - \Gamma \Delta P)|t|^{-\gamma} = Bt^{-\gamma} , \quad \text{(A2)}$$

where A and Γ are constants. This relation is valid for $\Delta\rho/\rho \ll 1$. We note that since ΔP is nearly constant, then by the proper choice of ΔT, the amplitude of the divergence can be made to vanish.

Data were taken with the main ^{4}He bath at several controlled temperatures to provide runs with different alues for ΔT. The results in Fig. 4 show that the amplitude of the effect is indeed linear in T as expected from (A2) and that near 3.47 K, the lines intersect. The data for our run closest to this temperature, namely 3.5 K, were shown in Fig. 2.

To determine how much of the experimental anomaly $\delta\epsilon \approx 1.5 \times 10^{-7}$ (see Fig. 2), is attributable to the compressibility thermal gradient effect, we calculate $(\partial\epsilon/\partial t)$ due to this effect from the linear model[13] and compare it with the data. We find that the data in Fig. 2 can be described very well by the instrumental effect as shown in Fig. 5. The coefficient B was obtained from the fit to the data. For an assumed $h = 0.5$ mm, one finds $\Delta T \approx 1$ μK, a reasonable value that corresponds to a calculated heat leak of 1 μW.

Since there does not seem to be any systematic deviation between the calculated and the experimental curve, we can put an upper bound for a real anomaly only slightly larger than the resolution of the bridge 1×10^{-8}. However, since we have had to subtract out a small pressure effect and the scatter in the data was a few parts in 10^8, we place a more conservative upper limit of about 4×10^{-8} on the dielectric constant anomaly.

The similarity between the SF_6 data[6] and the instrumental effect we found with the bath at 4.2 K is shown in Fig. 6. The scales have been shifted to em-

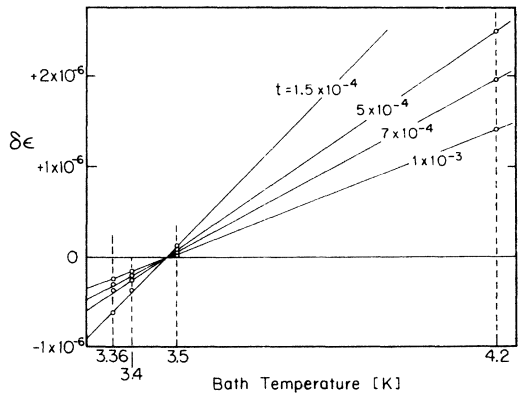

FIG. 4. Change $\delta\epsilon$ vs the bath temperature. One notes that $\delta\epsilon$ depends linearly on the difference between the cell temperature and the bath temperature.

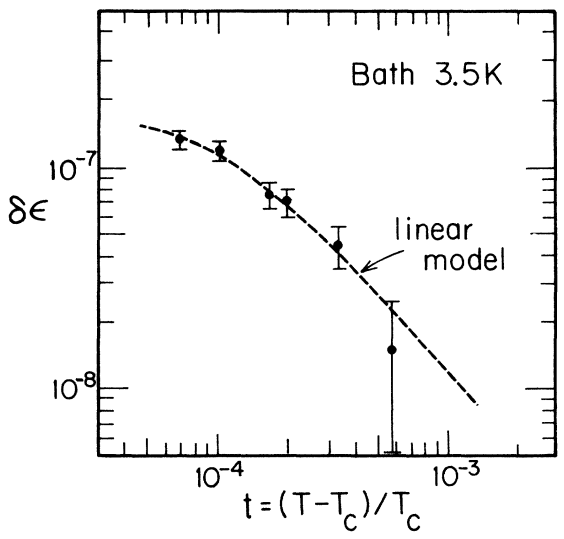

FIG. 5. Effect calculated from the "linear model" (Ref. 13), compared to the 3.5-K bath-temperature data.

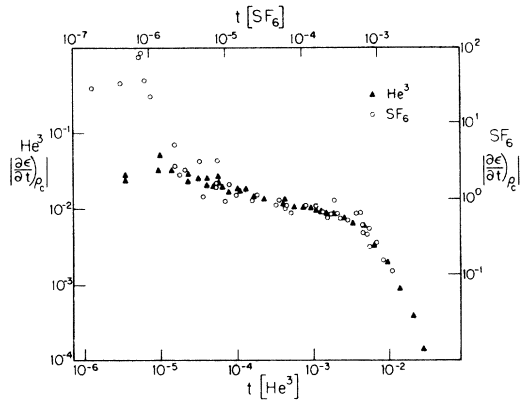

FIG. 6. Comparison of $(\partial\epsilon/\partial t)_{\rho_c}$ for ^{3}He and SF_6. The SF_6 temperature scale and amplitude scale are shifted to show that the two data sets have nearly identical shapes. ^{3}He data were taken with the main bath at 4.2 K.

phasize the similarity in shapes. Except for the lowest temperatures ($t < 10^{-5}$) the curves are almost identical. It would be plausible to attribute the difference in magnitudes to a larger percentage of gas outside the cell for the SF_6 experiment. However, only 0.3% of the fluid was contained in the capillary,[14] and hence this cannot explain the difference between the SF_6 and the ^{3}He data in their scaled representation. The difference in the temperature scales implies a larger pressure/thermal gradient in the ^{3}He experiment when the bath is at 4.2 K.

In summary, while the scaled behavior of the SF_6 and the ^{3}He data (with bath at 4.2 K!) is suggestive that the instrumental effects described above are important in both experiments, our opinion is that Hocken *et al.*[6] were well aware of such problems and accordingly careful in their measurements. Hence we are unable to draw any firm conclusions as far as the SF_6 data are concerned.

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