Compressed Liquid Densities, Saturated Liquid Densities, and Vapor Pressures of Hexafluoro-1,3-butadiene (C_4F_6)

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Hexafluoro-1,3-butadiene (Sifren 46, Ausimont; ASHRAE Code R2316) is a fluoro compound with two double bonds in the molecule (C_4F_6) showing very high performance for plasma, ion beam, or sputter etching in semiconductor devices' manufacturing. Vapor pressures and compressed liquid densities of hexafluoro-1,3-butadiene have been measured at temperatures ranging from (263 to 343) K with pressures up to 7000 kPa. Saturated liquid densities have been extrapolated from isothermal compressed liquid density data. Vapor pressure has been measured by means of an apparatus based on a glass equilibrium cell, while density has been measured with a vibrating tube densimeter (Anton Paar DMA 512). For the vapor pressure measurements, the estimated accuracy is ±1 kPa for pressure and ±0.02 K for temperature. For the density measurements, the estimated accuracy is ±0.02 K for temperature and ±3 kPa for pressure. The densimeter has been calibrated by using 1,1,1,2-tetrafluoroethane (R134a) and vacuum. The overall estimated accuracy for the density data is within ±0.1%.

1. Introduction

Hexafluoro-1,3-butadiene is a new colorless, odorless, toxic, flammable gas suitable for semiconductor plasma etching, with very high performance especially in plasma dielectric etching with Xe and Ar as carrier gases and dilutants. In fact, since in plasma dielectric etching it is essential to control the plasma chemistries in order to balance etching and deposition species, with C_4F_6 it is possible to achieve superior results over those with other gases, such as C_4F_8. Moreover, due to the short atmospheric lifetime (<1 day), negligible global warming potential, and inertness to the stratospheric ozone layer, it is also an environmentally compatible fluid.[1] Nevertheless, this fluid is almost unknown, and especially equilibrium and *PVT* properties are required. In this paper, hexafluoro-1,3-butadiene vapor pressures and compressed and saturated liquid densities are reported. Vapor pressure data range from 273.15 K to 343.15 K, while liquid density has been measured in the range between 263.15 K and 333.15 K, for vapor pressures up to 7000 kPa.

2. Experimental Section

2.1. Materials. Hexafluoro-1,3-butadiene, with no impurities detected by gas chromatography using both the flame ionization detector (FID) and the thermal conductivity detector (TCD), was supplied by Ausimont. R134a was used as a calibration fluid for the density measurement. It was supplied by ICI, and no impurities were detected by the FID and the TCD.

To eliminate the noncondensable gases, each sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing, and ultrasound. The samples were then used with no further purification.

2.2. Vapor Pressure Apparatus. A scheme of the apparatus used to measure the vapor pressure, already described,[2] is shown in Figure 1. The glass equilibrium cell had a volume of about 15 cm^3. The temperature of the thermostating fluid was controlled with an HAAKE N6 series thermostat with an auxiliary thermostatic bath to produce cooling. The bath temperature stability was estimated to be within ±0.01 K all along the measurements.

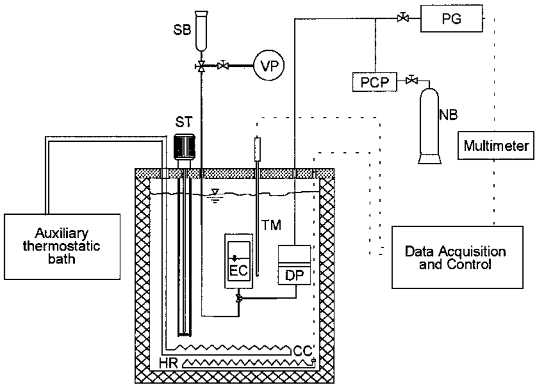

Figure 1. Vapor pressure measurements' apparatus scheme: CC, cooling coil; DP, diaphragm; EC, equilibrium cell; HR, heating resistance; NB, nitrogen bottle; PCP, pressure control pack; PG, pressure gauge; SB, sample bottle; ST, stirrer; TM, thermometer; VP, vacuum pump.

Temperature was measured by means of a 100 Ω platinum resistance thermometer with an overall estimated accuracy of ±0.02 K.

Pressure was measured with a digital pressure gauge with a full scale of 3500 kPa. The pressure inside the cell is transferred to a membrane-type differential pressure cell immersed in the thermostatic bath used to separate the chemicals from the quartz sensor of the pressure gauge. Nitrogen gas was used to balance the pressure at the membrane by a null detector. The estimated overall accuracy in the pressure measurement is ±1 kPa.

2.3. Compressed Liquid Density Apparatus. The compressed liquid density was measured using a stainless steel vibrating U-tube (Anton Paar DMA 512). A scheme of this apparatus is shown in Figure 2. The densimeter was

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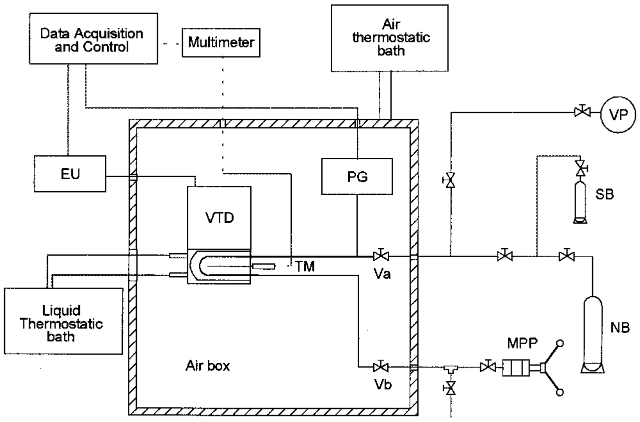

Figure 2. Density measurements' apparatus scheme: EU, evaluation unit; MPP, manual piston pump; NB, nitrogen bottle; PG, pressure gauge; SB, sample bottle; TM, thermometer; Va, Vb, on–off valves; VP, vacuum pump; VTD, vibrating tube densimeter.

Table 1. Total Uncertainty in the Density Measurements

Uncertainty of Pressure Measurements in kPa	
accuracy of the pressure gauge	±2
stability	±1
total	±3
Uncertainty of Temperature Measurements in K	
accuracy of thermometer	±0.020
stability of the thermostatic bath	±0.003
total	±0.023
Uncertainty of Period of Oscillation Measurements in μs	
variation	0.020
accuracy in counter	0.001
total	0.021
Uncertainty of the Calibration of Eq 1 in kg·m^{-3}	
uncertainty of the equation of state	0.70
influence of the period of oscillation fluctuations under vacuum	0.10
deviation from eq 1	0.10
total	0.90
Uncertainty in Density Calculation in kg·m^{-3}	
uncertainty in pressure measurements	0.06
uncertainty in temperature measurements	0.06
uncertainty in period of oscillation measurements	0.10
uncertainty of the calibration equation	0.90
total	1.12

Table 2. Experimental Vapor Pressure Data for Hexafluoro-1,3-butadiene

T/K	P/kPa	T/K	P/kPa
273.15	81	308.15	295.1
278.15	99.5	313.15	346.1
278.62	101.3	318.15	402.6
283.15	121.7	323.15	466.3
288.15	147.5	328.15	537.3
293.15	176.8	333.15	616.3
298.15	211.5	338.15	703.5
303.15	250.6	343.15	799.3

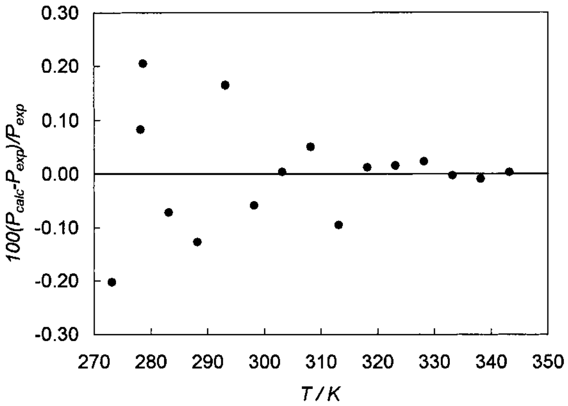

Figure 3. Vapor pressure deviations of the experimental data for hexafluoro-1,3-butadiene from eq 2.

Table 3. Coefficients of Eq 2 Regressed from Vapor Pressure Data

coefficient	numerical value
A_1	5.9108
A_2	2.2616
A_3	0.9214
A_4	−15.0786

Table 4. Critical Constants for Hexafluoro-1,3-butadiene

T_c/K	P_c/kPa	ρ_c/kg·m^{-3}
412.8	3188	504.8

connected to an electronic evaluation unit for the measurement of the period of oscillation of the tube (Anton Paar mPDS 2000). The sample was charged in the U-tube by means of stainless steel tubes connecting the cell to the pure refrigerant bottle. The fluid was pressurized into the vibrating tube by means of a manual piston pump (RUSKA T1200V). Pressure was measured with a differential pressure gauge (Druck DPI 145) with a scale-up to 7000 kPa. The uncertainty in the pressure measurement was estimated to be within ±3 kPa.

The temperature of the vibrating tube was stabilized by circulating a water/ethylene glycol solution, coming from an external thermostated bath, through a heat exchanger surrounding the U-tube. The heat exchanger was insulated to reduce the influence of the external ambient. A stability of ±0.003 K all along the measurements was achieved.

After charging and pressurizing the sample, the two on–off valves (Va) and (Vb) were shut to get a closed circuit including the heat exchanger surrounding the U-tube and the manometer. To avoid the influence of the oscillation in ambient temperature on the measuring pressure, the closed circuit was enclosed in an air thermostatic bath that allowed us to keep a temperature of (298.15 ± 0.05) K around the circuit.

The temperature at the vibrating tube was measured with a PT 100 Ω resistance thermometer connected to a HP 3458A multimeter. The estimated uncertainty in the temperature measurement was within ±0.02 K.

The density was determined on the basis of the period of oscillation measurement of the tube filled with a pure sample. In fact, the following relationship between period of oscillation T and density ρ is valid:[3]

$$T^2 = A\rho + B$$

Then A and B are considered as apparatus constants, and they must be determined from calibration measurements. These constants are actually dependent on temperature, which influences the thermal expansion coefficient and the elastic constant of the vibrating tube, and pressure, which influences the elastic response of the vibrating tube.

The calibration at a given temperature was performed by measuring the vibrating U-tube period of the empty tube and of the tube filled with R134a at four different pressures.

At isothermal conditions the constant B depends only on the oscillation period under vacuum, while the constant A is dependent on pressure.

Table 5. Experimental *PVT* Data for Hexafluoro-1,3-butadiene

ρ/kg·m^{-3}	P/kPa	T/K	ρ/kg·m^{-3}	P/kPa	T/K	ρ/kg·m^{-3}	P/kPa	T/K
1518.5	313.1	263.72	1425.5	353.3	293.40	1317.0	462.9	323.17
1519.0	499.1	263.71	1426.1	536.3	293.40	1317.6	532.8	323.22
1520.4	993.4	263.72	1428.2	1005.2	293.40	1318.8	707.6	323.17
1523.1	1937.5	263.72	1432.6	2039.9	293.40	1321.0	1011.7	323.17
1526.3	3086.3	263.72	1436.5	2975.7	293.41	1327.9	2000.7	323.17
1528.9	4028.2	263.72	1440.9	4079.8	293.40	1334.7	3032.2	323.17
1531.8	5058.7	263.72	1444.6	5041.1	293.40	1341.0	4024.0	323.17
1534.7	6128.9	263.72	1448.5	6045.3	293.40	1346.9	5022.3	323.17
1537.2	7065.6	263.72	1452.1	7012.2	293.40	1352.2	5971.2	323.17
						1358.2	7085.6	323.17
1489.2	302.4	273.55	1391.9	347.4	303.29			
1490.0	527.4	273.55	1392.8	533.8	303.30	1278.7	739.2	333.07
1491.8	1084.1	273.55	1395.5	1052.9	303.30	1281.0	1003.2	333.07
1495.1	2068.5	273.55	1400.3	2042.1	303.30	1289.5	2020.1	333.07
1498.2	3036.1	273.55	1405.1	3049.2	303.30	1297.4	3024.7	333.07
1501.3	4036.0	273.55	1409.6	4033.8	303.30	1304.9	4033.2	333.07
1504.3	5022.2	273.55	1414.2	5049.0	303.29	1311.8	5029.6	333.07
1507.2	5999.6	273.55	1418.3	6019.6	303.29	1318.4	6023.8	333.07
1510.2	7016.2	273.55	1422.4	7012.3	303.29	1324.5	6986.9	333.07
1457.9	325.3	283.49	1355.3	501.7	313.29			
1458.8	548.3	283.49	1358.5	1027.7	313.29	1237.0	940.9	342.98
1460.7	1039.0	283.49	1364.3	2027.2	313.29	1238.0	1020.2	342.97
1464.5	2027.1	283.49	1369.9	3052.2	313.29	1248.2	1996.4	342.97
1468.1	3026.0	283.49	1375.1	4014.8	313.29	1258.1	3029.4	342.98
1471.6	3993.4	283.48	1380.2	5009.7	313.29	1267.0	4029.4	342.98
1475.3	5061.9	283.48	1385.1	6014.2	313.29	1275.3	5033.1	342.98
1478.6	6039.4	283.48	1390.0	7044.4	313.29	1283.1	6022.8	342.98
1481.7	7013.5	283.48	1356.8	736.5	313.29	1290.0	6979.1	342.98

The calibration curve actually applied at constant temperature was the following:

$$T^2 = (aP^2 + bP + c)\rho + B \qquad (1)$$

The measured oscillation period was correlated to the known density of R134a at four pressures, regressing the coefficients a, b, and c in eq 1. The equation proposed by Tillner-Roth et al.[4] was used to determine the R134a density at the calibration pressure and temperature.

The total uncertainty of this apparatus, evaluated taking into account the influence of temperature, pressure, period of oscillations, and R134a EoS uncertainties, is around 1.2 kg/m^3, as shown in Table 1.

3. Results

3.1. Vapor Pressure. Sixteen vapor pressures were measured from (273.15 to 343.15) K; the results are reported in Table 2.

A vapor pressure correlation was developed on the basis of these experimental data, using a Wagner type equation in the form[5]

$$\ln\left(\frac{P}{P_c}\right) = \frac{T_c}{T}(A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^6) \qquad (2)$$

where

$$\tau = 1 - \frac{T}{T_c}$$

The coefficients were regressed by minimizing the objective function with a simplex search method, using the same weight for all the data. The same method was applied to find the coefficients for eqs 3 and 8. The regressed A_i values are reported in Table 3, and the critical constants, in Table 4.[6] Considering the uncertainty in the critical parameters, the correlation is reliable only within the experimental temperature range.

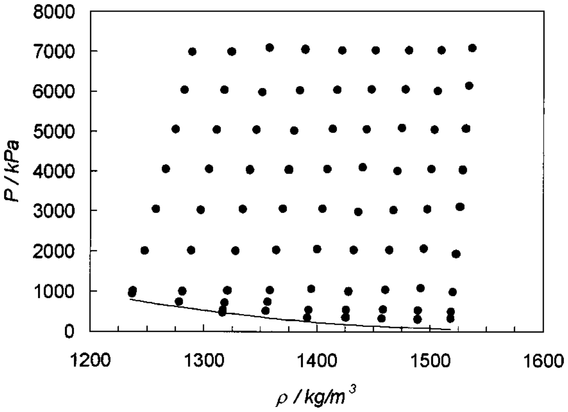

Figure 4. Experimental compressed liquid density data (●) and calculated saturated liquid density (—) for hexafluoro-1,3-butadiene.

The vapor pressure deviations between experimental data and eq 2 are shown in Figure 3. The standard deviation is ±0.1%.

3.2. Compressed Liquid Density. A total of 80 compressed liquid density data points were measured at nine isotherms in the range between 263 K and 333 K, for at least eight pressures per isotherm ranging from a pressure slightly above saturation to 7000 kPa. These data are summarized in Table 5. Figure 4 shows their distribution on the (ρ, P) plane and the saturated liquid density line.

The results were fitted to a generalized Tait equation in the form proposed by Thomson et al.: [7]

$$V = V_s\left(1 - c\ln\frac{\beta + P}{\beta + P_s}\right) \qquad (3)$$

where V is the molar volume, V_s is the saturated molar volume, P is the pressure, and P_s is the vapor pressure at a given temperature. The terms β and c are obtained from

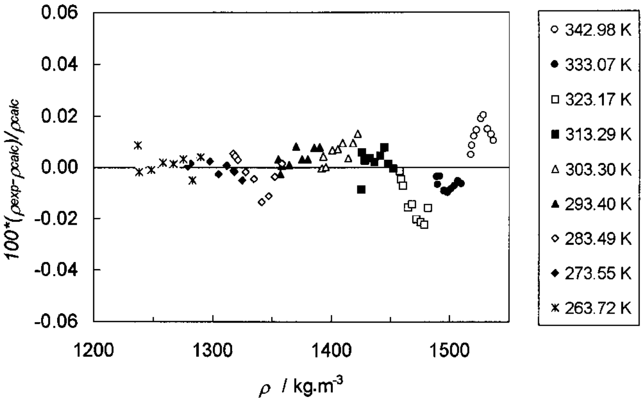

Figure 5. Density deviations of the experimental data from the generalized Tait equation.

Table 6. Coefficients of the Generalized Tait Equation for Hexafluoro-1,3-butadiene

coefficient	numerical value
a	$-8.938\,180\,736\,737\,89 \times 10^{1}$
b	$4.956\,106\,772\,228\,92 \times 10^{2}$
c	$7.919\,131\,526\,056\,01 \times 10^{-2}$
d	$-9.350\,273\,97\,5608\,69 \times 10^{2}$
e	$6.361\,107\,435\,261\,68 \times 10^{2}$
f	$6.921\,635\,463\,214\,63$
g	$-9.580\,101\,309\,572\,38 \times 10^{-2}$
h	$-4.192\,790\,499\,606\,04$
j	$-9.240\,221\,080\,906\,75 \times 10^{-2}$
k	$5.324\,914\,441\,268\,51 \times 10^{-1}$

the following equations:

$$\beta = P_c[-1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3}] \quad (4)$$

$$e = \exp(f + g\omega + h\omega^2) \quad (5)$$

$$c = j + k\omega \quad (6)$$

Here ω is the acentric factor calculated through the basic equation

$$\omega = -\log P_{sr}(\text{at } T_r = 0.7) - 1 = 0.322\,25 \quad (7)$$

where P_{sr} is the reduced vapor pressure at the reduced temperature $T_r = 0.7$.

The *a*...*k* coefficients, regressed on the basis of the experimental data, are given in Table 6.

Equation 3 allows a good representation of the experimental data, as shown by Figure 5, where the deviations between the calculated and the experimental data are reported. The measured compressed liquid densities are reproduced with a standard deviation of ±0.01%.

Table 7. Extrapolated Saturated Liquid Density of Hexafluoro-1,3-butadiene and Coefficients Regressed for Eq 8

T/K	P/kPa	ρ_{sat}/kg·m^{-3}
263.72	53.1	1517.8
273.55	82.2	1488.4
283.49	123.2	1457.1
293.40	178.7	1424.6
303.30	251.8	1391.4
313.29	347.3	1354.4
323.18	466.7	1317.1
333.07	615.0	1277.6
342.98	795.9	1235.5

A	B	C	D
3.633 438 196	−7.059 711 35	13.399 588 45	−7.153 950 62

3.3. Saturated Liquid Density. The saturated liquid density was determined by extrapolating each isotherm at the vapor pressure using a third-degree polynomial; the vapor pressures were calculated with eq 2. All these data, reported in Table 7, were regressed with an equation in the form

$$\rho_s = \rho_c(1 + A\tau^{1/3} + B\tau^{2/3} + C\tau + D\tau^{4/3}) \quad (8)$$

where $\tau = 1 - T/T_c$. Also, the coefficients for eq 4 are reported in Table 7. The absolute average deviation between eq 8 and the extrapolated saturated liquid densities is 0.03%,

4. Conclusion

In this paper the vapor pressure and the liquid density of the new compound hexafluoro-1,3-butadiene have been studied. Sixteen vapor pressures were measured from (273.15 to 343.15) K, and eighty compressed liquid density data points were measured along nine isotherms in the range between (263 and 333) K. Both sets of data were correlated with a proper equation. The saturated liquid density has been calculated at the experimental temperatures by extrapolating the liquid density isotherms to the vapor pressure calculated with a Wagner equation. The saturated liquid densities have been correlated with a four-parameter equation in the reduced form.

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