

# Vapor Pressures of Hexafluoroethane and Octafluorocyclobutane

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We have used a static cell to measure vapor pressures of hexafluoroethane ( $C_2F_6$ ) and octafluorocyclobutane (cyc- $C_4F_8$ ). Measurements for hexafluoroethane were made over the temperature range 177 to 291 K; pressures ranged from 35 to 2902 kPa. Measurements for octafluorocyclobutane were made over the temperature range from 234 to 387 K; pressures ranged from 21 to 2698 kPa. Sample purity was 99.999 molar % or greater for both compounds.

## Introduction

Hexafluoroethane ( $C_2F_6$ ) has been used in the past as a low-temperature refrigerant, but this application is now quite limited. Most of the  $C_2F_6$  produced today is of high purity and used as a plasma process gas in thin-film etching or chemical vapor deposition during the manufacture of semiconductors and other microelectronic devices. Octafluorocyclobutane (cyc- $C_4F_8$ ) has previously been used as a refrigerant, propellant, and blowing agent, but today it is also finding new uses in advanced semiconductor manufacturing processes. In these electronics applications, high purity and product consistency are extremely important, and material produced today routinely exceeds 99.999 molar % purity.

The vapor pressure of  $C_2F_6$  has been investigated by a number of researchers in the past (Pace and Aston, 1948; Kijima et al., 1977; Leu and Robinson, 1989), but the experimental results were not in good agreement with our own published data (DuPont, 1961) or with our more recent limited experimental data which have not been published. Similarly, a number of researchers (Whipple, 1952; Furukawa et al., 1954; Douslin et al., 1959; Martin, 1962) have reported vapor pressures for cyc- $C_4F_8$ , but their results are either limited in temperature range (Furukawa, Douslin) or vary quite widely (Whipple, Martin). Since DuPont is a producer of both  $C_2F_6$  and cyc- $C_4F_8$ , and since earlier researchers, including our own, did not have access to the ultrahigh-purity materials available today, we decided to perform more-detailed studies of  $C_2F_6$  and cyc- $C_4F_8$  vapor pressures.

The following three sections describe the materials used and the apparatus and techniques employed to measure  $C_2F_6$  and cyc- $C_4F_8$  vapor pressures. The next two sections present the results of these measurements and compare them with earlier published data.

## Experimental Section

**Materials.** The hexafluoroethane ( $C_2F_6$ ) and octafluorocyclobutane (cyc- $C_4F_8$ ) were manufactured by DuPont. The  $C_2F_6$  was >99.9999 molar % organic purity, and the cyc- $C_4F_8$  was >99.999 molar % organic purity.

“Organic purity” refers to halocarbon impurities, excluding water and inerts. Both materials contained <1 ppm

(molar) water, and both were degassed prior to making the measurements.

**Hexafluoroethane Measurements.** Roughly 20 g of  $C_2F_6$  was transferred from a manufacturing cylinder to an evacuated 30 cm<sup>3</sup> stainless steel equilibrium cell which was immersed in liquid nitrogen during the transfer. Material in the equilibrium cell was degassed by repeated freeze–pump–thaw cycles using liquid nitrogen to freeze the material. The equilibrium cell containing degassed material was then immersed in a constant-temperature bath, and the temperature of the bath and the vapor pressure were measured. The pressure was measured using Paroscientific pressure transducers with 0.01% accuracy, Model 740-45A (for pressures <310 kPa) and Model 740-1K (for higher pressures). The temperature was measured using a Hart Scientific Black Stack Base Unit with 0.007 K accuracy and a secondary PRT with 0.01 K accuracy (ITS-90 scale). Four temperature baths were used in these experiments. A Neslab RTE-111D bath with a stability of 0.01 K was used for temperatures >248 K. A Neslab ULT-80D bath with a stability of 0.03 K was used for temperatures between 248 K and 197 K. For measurements with  $C_2F_6$  at 184 K and 177 K, slurry baths of isopropyl alcohol/liquid nitrogen and acetone/liquid nitrogen were used. The apparatus used in this work has been described previously (Kao et al., 1997).

**Octafluorocyclobutane Measurements.** Transfer and degassing of the cyc- $C_4F_8$  was done by the same procedure as described above, except roughly 50 g of material was used with an 85 cm<sup>3</sup> equilibrium cell. The pressure was measured using Paroscientific pressure transducers with 0.01% accuracy, Model 740-45A (for pressures <310 kPa) and Model 740-100A (for pressures between 310 and 689 kPa). A Heise pressure transducer with 0.035% accuracy, Model 901B, was used for pressures up to 2700 kPa. Vapor pressure for cyc- $C_4F_8$  at temperatures above ambient was measured indirectly using a Ruska high-temperature differential pressure null detector, Model 2439-702, with a Control box, Model 2416-711. The null detector and parts between the detector and the equilibrium cell were heated to at least 453 K to avoid condensation. Three temperature baths were used in these experiments. A Lauda RK20 bath with a stability of 0.01 K was used for temperatures below 293 K, a Neslab RTE-110 bath with a stability of 0.01 K was used for temperatures between 293 K and 343 K, and a Neslab EX-250HT bath with a stability of 0.02 K was used for temperatures above 343 K.

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**Table 1. Experimental Vapor Pressure Data for Hexafluoroethane (C<sub>2</sub>F<sub>6</sub>)**

<i>T</i> /K	<i>P</i> /kPa	<i>T</i> /K	<i>P</i> /kPa
177.28	34.87	213.11	243.2
177.28	34.89	213.11	243.5
177.29	34.98	213.15	243.7
177.57	35.54	213.15	243.7
177.59	35.63	213.15	243.7
177.60	35.67	218.15	302.2
177.65	35.75	223.09	369.6
177.67	35.80	228.11	448.8
177.71	35.89	233.10	539.4
177.75	35.86	238.12	643.6
184.15	54.28	243.12	761.4
184.22	54.38	248.16	896.5
184.23	54.40	253.10	1044.9
184.41	55.19	258.11	1213.9
184.89	56.41	263.12	1402.7
196.62	110.1	268.10	1610.8
196.62	110.1	273.14	1842.1
196.62	110.1	278.15	2099.5
196.76	110.8	283.15	2383.1
197.08	112.9	288.20	2699.8
199.88	130.3	288.21	2697.4
200.09	131.6	289.15	2761.5
203.06	152.6	290.17	2831.0
203.11	153.0	291.18	2902.3
203.14	153.5	291.19	2902.5
208.08	193.7	291.19	2902.4
208.13	195.0	291.20	2902.1
208.14	194.6		

## Results and Discussion

**Hexafluoroethane.** A total of 55 experimental measurements were made with temperatures from 177 to 291 K and experimental pressures from 35 to 2902 kPa. The unsmoothed experimental data are shown in Table 1. No adjustments were made for sample purity because the C<sub>2</sub>F<sub>6</sub> used in this work contained no inerts, <1 ppm molar of other organic impurities, and <1 ppm molar of water.

The data were correlated with a four-term Cragoe equation of the form

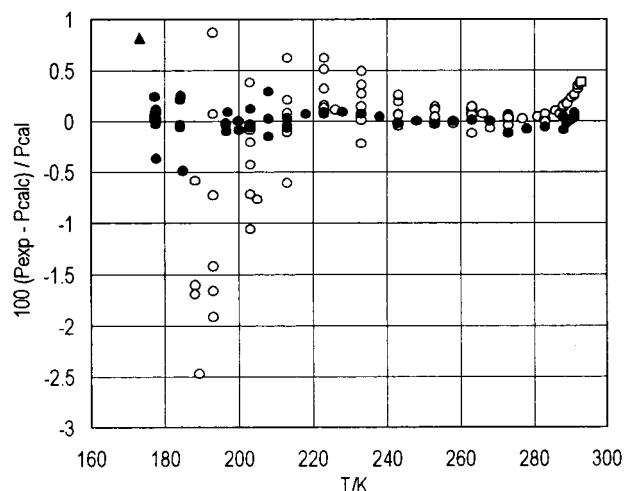
$$\ln P = A + B/T + CT + DT^2 \quad (1)$$

where  $A = 23.855\,755$ ,  $B = -2714.8507$ ,  $C = -0.036\,895\,822$ , and  $D = 4.934\,326\,1 \times 10^{-5}$  with pressure  $P$  in kPa and temperature  $T$  in kelvin.

Our highest temperature experimental data points were at approximately 291 K, which is lower than the critical temperature of 293.035 K reported by Saikawa et al. (1979). Equation 1 gives a critical pressure of 3030.47 kPa at 293.035 K, whereas Saikawa et al. calculated 3042.00 kPa at this temperature using the vapor pressure correlation of Kijima et al. (1977).

Our lowest temperature experimental data points were measured at about 177.3 K. Aldersley et al. (1979) measured a vapor pressure of 26.38 kPa at 173.11 K, which is the triple-point temperature reported by Pace and Aston (1948). Equation 1 extrapolates to a pressure of 26.17 kPa at a temperature of 173.11 K.

Figure 1 shows the deviation of our data from eq 1, as well as those of Kijima et al. (1977), which appear to be the best experimental data currently available in the literature. There is good agreement with Kijima et al. above 240 K. Below 240 K, there is more scatter in the data of Kijima et al. and the agreement with our data is not as good. The critical temperature of Saikawa et al. (1979) and the triple-point temperature of Aldersley et al. (1979) are also shown in Figure 1.



**Figure 1.** Hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) deviations of the data from eq 1: (●) this work; (□) critical temperature, Saikawa et al. (1979); (▲) triple-point temperature, Aldersley et al. (1979); (○) Kijima et al. (1977).

**Table 2. Vapor Pressure Data for Ethylene**

<i>T</i> /K	<i>P</i> <sub>exp</sub> /kPa	<i>P</i> <sub>calc</sub> <sup>a</sup> /kPa	<i>P</i> <sub>diff</sub> /%
177.51	159.2	159.46	-0.14
177.51	159.2	159.46	-0.15
177.50	159.2	159.37	-0.11
177.50	159.2	159.37	-0.12
177.48	159.0	159.20	-0.12
177.48	159.0	159.20	-0.12
177.48	159.0	159.20	-0.13

<sup>a</sup> Calculated with eq 2.

The temperature of the normal boiling point of C<sub>2</sub>F<sub>6</sub> was found to be 195.06 K (-78.09 °C) by using eq 1.

To check on the accuracy of the slurry baths used for the low-temperature C<sub>2</sub>F<sub>6</sub> measurements, we also measured the vapor pressure of ethylene using the acetone/liquid nitrogen slurry bath. Seven experimental vapor pressure points for ethylene were measured at nominal temperatures near 177.5 K. The experimental results are shown in Table 2 and are compared with ASHRAE data (1993) for ethylene over the temperature range 127.59 to 282.32 K (3.39 to 5040.1 kPa). The data were fitted for this work with a five-term Cragoe equation of the form

$$\ln P = A + B/T + CT + D \ln T + ET^2 \quad (2)$$

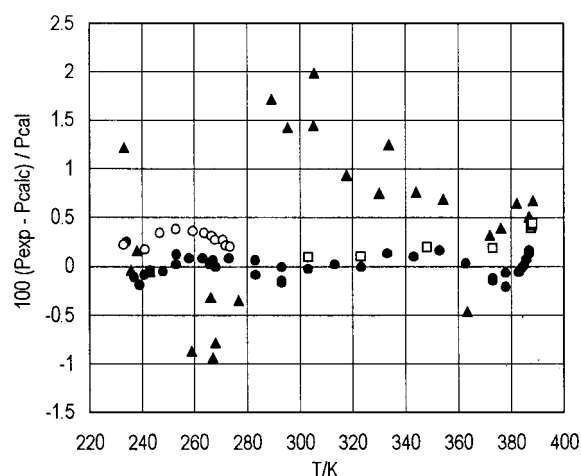
where  $A = 44.366\,447$ ,  $B = -2408.1962$ ,  $C = -0.002\,175\,543\,60$ ,  $D = -5.015\,614\,4$ , and  $E = 2.012\,261\,40 \times 10^{-5}$  with pressure  $P$  in kPa and temperature  $T$  in kelvin.

Our vapor pressure measurements for ethylene differ by 0.15% or less from accepted values. The purity of the ethylene used for this work was 99.914%; the sample was degassed using the same technique which was used for C<sub>2</sub>F<sub>6</sub>. Since the specific impurity in the ethylene was not known, we cannot say with certainty whether the small errors are due to impurities or to experimental technique.

**Octafluorocyclobutane.** A total of 36 experimental measurements were made with temperatures from 234 to 387 K and experimental pressures from 21 to 2698 kPa. The unsmoothed experimental data are shown in Table 3. No adjustments were made for sample purity because the cyc-C<sub>4</sub>F<sub>8</sub> contained <10 ppm molar of other organic impurities and <1 ppm molar of water. The data were correlated with

**Table 3. Experimental Vapor Pressure Data for Octafluorocyclobutane (cyc-C<sub>4</sub>F<sub>8</sub>)**

<i>T</i> /K	<i>P</i> /kPa	<i>T</i> /K	<i>P</i> /kPa
234.23	20.51	293.21	265.2
237.12	24.01	303.24	366.1
239.17	26.82	313.25	492.7
241.12	29.79	323.22	648.4
243.19	33.22	333.25	841.0
248.16	42.71	343.19	1069.5
253.19	54.48	353.04	1340.6
253.24	54.67	362.98	1661.2
258.07	68.26	373.17	2048.4
263.21	85.56	373.20	2049.1
266.10	96.66	378.06	2260.5
267.13	100.9	378.07	2258.0
268.15	105.2	383.09	2495.8
273.24	129.2	384.16	2549.4
283.22	188.1	385.10	2597.1
283.25	188.0	386.10	2649.2
293.17	265.3	387.01	2698.4
293.21	265.3	387.01	2697.7

**Figure 2.** Octafluorocyclobutane (cyc-C<sub>4</sub>F<sub>8</sub>) deviations of the data from eq 3: (●) this work; (○) Furukawa et al. (1954); (▲) Martin (1962); (□) Douslin et al. (1959).

a five-term Cragoe equation of the form

$$\ln P = A + B/T + CT + D \ln T + ET^2 \quad (3)$$

where  $A = -98.499\,002$ ,  $B = -1805.4910$ ,  $C = -0.117\,203\,75$ ,  $D = 24.247\,841$ , and  $E = 7.973\,565\,2 \times 10^{-5}$  with pressure  $P$  in kPa and temperature  $T$  in kelvin.

Our highest temperature experimental data point was at 387.01 K, which is lower than the critical temperature of 388.37 K reported by Douslin et al. (1959). Equation 3 gives a critical pressure of 2765.38 kPa at 388.37 K, whereas Douslin et al. calculated 2777.53 kPa at this temperature.

Our lowest experimental data point was measured at 234.23 K. Furukawa et al. (1954) measured the triple-point temperature of 232.96 K and calculated a vapor pressure of  $19.04 \pm 0.04$  kPa at this temperature. Equation 3 extrapolates to a pressure of 19.03 kPa at a temperature of 232.96 K.

Figure 2 shows the deviation of our data from eq 3, as well as those of Furukawa et al. (1954), Douslin et al.

(1959), and Martin (1962). Individually, the temperature ranges of the data of Furukawa et al. and Douslin et al. are quite limited, but taken together, their combined data are in good agreement with our own. The data of Martin cover approximately the same temperature range as ours, but there is considerably more scatter in Martin's data, particularly below about 310 K.

The temperature of the normal boiling point of cyc-C<sub>4</sub>F<sub>8</sub> was found to be 267.24 K ( $-5.91$  °C) by using eq 3. Furukawa et al. reported a normal boiling point of 267.17 K ( $-5.98$  °C).

### Summary

We have made vapor pressure measurements for hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) over the temperature range 177 to 291 K and for octafluorocyclobutane (cyc-C<sub>4</sub>F<sub>8</sub>) over the temperature range 234 to 387 K. Sample purity was >99.999 molar % for both materials. We believe the data for C<sub>2</sub>F<sub>6</sub> are more accurate than any previous data reported in the literature. Our data for cyc-C<sub>4</sub>F<sub>8</sub> are in good agreement with the best data available in the literature but cover a wider temperature range.

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