The Vapor Pressure of Hexafluoro and Pentafluorochloroacetone

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The vapor pressures of hexafluoroacetone and pentafluorochloroacetone have been measured from −35° C. to their critical temperatures, and fitted to a four constant equation. The average deviation for the hexafluroacetone data is ±0.16% and for the pentafluorochloroacetone, ±25%. The critical temperatures of the compounds were also determined.

HEXAFLUOROACETONE is an interesting organic compound from both a practical and theoretical point of view. Although there has been extensive investigation and numerous publications concerning its reactions, little is known concerning its physical properties (2).

The pentafluorochloroacetone, the next number in the homologous series is chemically similar to the perfluorinated acetone. Data on the physical properties of this compound are also lacking.

EXPERIMENTAL

Sample Purity. Samples of both the hexafluoroacetone and the pentafluorochloroacetone were obtained from the Baton Rouge Development Laboratory, General Chemical Division, Allied Chemical Corporation. The hexafluoroacetone was analyzed by vapor phase chromatography and showed 0.05% impurities. An analysis for HF and HCl showed < 100 p.p.m. for each. The sample was not purified further and is believed to be at least 99.9 mole % hexafluoroacetone.

The sample of pentafluorochloroacetone was distilled in a low temperature Podbielniak type still of about 30 theoretical plates and the center cut taken. An analysis by vapor phase chromatography showed 0.1% total impurities. The impurities are probably HCl, HF, and hexafluoroacetone. The purity of this sample is believed to be 99.9 mole %.

Since both of these compounds are very hygroscopic, they were dried by passing over Linde 4A molecular sieve prior to use.

Apparatus and Procedure. The critical temperature was determined by heating a sample in a sealed glass tube and then observing the average temperature of the disappearance and appearance of the meniscus (3). The amount of liquid in the tube was adjusted by trial and error so that two phases were present at temperatures just below the critical. The tube was heated in a stirred oil bath and the temperature measured by a chromel-constantan thermocouple. The thermocouple was calibrated at the critical temperature by a platinum resistance thermometer. The accuracy of the calibrated thermocouple was ±0.05° C.

The apparatus used for the vapor pressure measurements is similar to that previously used at this laboratory (1). The pressures below one atmosphere were measured with a mercury manometer. The height of the mercury column was measured by a cathetometer with an accuracy of better than ±0.1 mm. Two vapor pressure apparatus were used for measurements above atmospheric pressure, one using a 100 p.s.i. Hiese gauge readable to 0.1 p.s.i., the other using a 1000 p.s.i. Hiese gauge readable to 0.2 p.s.i. The gauges were calibrated against 12-inch Hiese gauges which in turn were calibrated by a Harwood dead weight tester. The accuracy of the gauges including calibration correction was better than 0.1% of the full scale reading.

All temperature measurements were made with a Leeds and Northrup platinum resistance thermometer sensitive to ±0.01° C. and accurate to ±0.03° C. The bath temperatures were controlled to better than ±0.03° C.

RESULTS

The experimental data were fitted to three forms of vapor pressure equations by the method of least squares. The three equations were:

$$\log P = A + (B/T) + (C/T^2) + D \log T \quad (1)$$

$$\log P = A + (B/T) + CT + D \log T \quad (2)$$

$$\log P = A + (B/T) + CT + DT^2 \quad (3)$$

For both sets of data, Equation 3 produced the smallest average deviation. The following Table shows the average and maximum percent deviations for the three equations.

	Equation (1)		Equation (2)		Equation (3)	
	% Av. Dev.	% Max. Dev.	% Av. Dev.	% Max. Dev.	% Av. Dev.	% Max. Dev.
Hexafluoroacetone	0.24	0.43	0.19	0.46	0.16	0.46
Pentafluorochloroacetone	0.33	0.69	0.28	0.65	0.26	0.75

For both compounds, Equation (1) showed the largest % deviation near the critical temperature while Equation (3) gave the best fit in that region. Equation (3) was chosen as best representing the data on the basis of the average deviation and its better fit in the critical region. The constants for this equation are given in Table I.

Table I. Constants of the Vapor Pressure Equation

$$\log P = A + (B/T) + CT + DT^2$$

	A	B	C	D
Hexafluoroacetone	+11.281636	−1813.956	−0.02149103	$+2.288914 \times 10^{-5}$
Pentafluorochloroacetone	+10.119514	−1933.812	−0.01559002	$+1.449813 \times 10^{-5}$

P = absolute pressure, atm.
T = absolute temperature, ° K. = ° C. + 273.16.
Table III shows the fit of the equations to the experimental data.

Table II. Comparison of Physical Constants of Hexafluoroacetone and Pentafluorochloroacetone

	CF_3COCF_3	CF_3COCF_2Cl
Critical Temperature	+84.1° C.	+137.5° C.
Critical Pressure[a]	28.04 atm.	28.40 atm.
Normal Boiling Point[a]	−27.5° C.	+7.8° C.
Freezing Point	−122° C.	−133° C.
Density at 25° C.	1.318 grams/cc.	1.430 grams/cc.

[a] Calculated from the vapor pressure equations.

Table III. Vapor Pressure

Temp., ° C.	Press. Obs., Atm.	Press. Calcd., Atm.	% Dev.[a]
	Hexafluoroacetone		
−33.31	0.7618	0.7602	+0.21
−27.19	1.0120	1.0130	−0.10
−22.35	1.254	1.256	−0.16
−8.81	2.17	2.18	−0.46
0.00	3.02	3.01	+0.33
+12.96	4.64	4.64	0.00
+20.70	5.89	5.89	0.00
+27.90	7.28	7.26	+0.27
+42.91	10.86	10.88	−0.18
+54.50	14.47	14.49	−0.14
+64.71	18.39	18.39	0.00
+72.95	22.08	22.10	−0.09
+79.82	25.66	25.62	+0.16
+83.72	27.87	27.82	+0.17
		Av. Dev.	±0.16
	Pentafluorochloroacetone		
−40.91	0.0902	0.0900	+0.22
−34.31	0.1332	0.1338	−0.45
−30.23	0.1683	0.1688	−0.30
−22.04	0.2634	0.2619	+0.57
−10.32	0.4670	0.4635	+0.75
0.00	0.7282	0.7300	−0.25
0.00[b]	0.7284	0.7300	−0.22
+13.52	1.245	1.248	−0.24
+29.68	2.19	2.20	−0.46
+31.76	2.35	2.35	0.00
+50.89	4.21	4.19	+0.47
+60.62	5.48	5.46	+0.36
+71.62	7.22	7.23	−0.14
+84.10	9.72	9.71	+0.10
+96.43	12.75	12.75	0.00
+107.63	16.08	16.10	−0.06
+117.90	19.71	19.72	−0.05
+125.83	22.92	22.93	−0.03
+132.17	25.82	25.79	+0.12
+136.27	27.83	27.78	+0.18
		Av. Dev.:	±0.25%

[a] $[(P_{obs.} - P_{cal.})/P_{obs.}] \times 100$. [b] Check run.

Table II compares some of the physical constants for the two ketones. The critical pressures were calculated by substituting the critical temperatures into the vapor pressure equations.

DISCUSSION

The only other vapor pressure data reported are that of Morse, Asycough, and Leitch (2) on hexafluoroacetone. Their data cover the range of −60° C. to −28° C. and are about 2% higher than the present data in the range of overlap.

The absolute accuracy of the pressure measurements in the present work varies from 0.05% for manometric points to about 0.75% in the lower ranges of the Bourdon gauges. To check the reproducibility, a completely independent run using a new portion of the sample was made on the pentafluorochloroacetone at 0° C. Table III shows that the vapor pressure checked to better than 0.03%.

Both ketones studied are difficult to obtain in a completely anhydrous condition and the presence of small amount of moisture in these samples is possible.

The equations derived from the present data are believed to have an overall accuracy of ±0.5% over the temperature range investigated.

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