Ethyl Fluoride Vapor Pressure

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The vapor pressure of ethyl fluoride was measured from 227.65 to 322.48K (0.6893–16.77 atm). The data were in agreement with literature vapor-pressure values that had been obtained over both a lower- and a higher-pressure range than the present work. A four-parameter vapor-pressure equation for ethyl fluoride was obtained by regressing the combined experimental data. The vapor pressure of ethyl fluoride is given by ln P = 66.4460 − 3939.51/T + 0.0159614T − 9.79050 ln T. In this equation, T is in K and P is in atmospheres. This equation fit the combined experimental data (0.01316–49.62 atm) to within an average error of 0.35% and a maximum error of 0.89%. The data are in agreement with the tabular values reported by the Thermodynamics Research Center Data Project but indicate an average vapor-pressure deviation greater than 30% for the values reported in the "Chemical Engineers' Handbook."

The normal boiling point of ethyl fluoride has been reported as 235.45K (−37.7°C) by Grosse (*2*) and by Grosse and Linn (*3*). Grosse et al. (*4*) tabulated six vapor pressures from 10 to 760 mm Hg but did not report the actual experimental data for this component. This source records the normal boiling point to be 236.05K (−37.1°C). Data from these three sources served as the basis for the ethyl fluoride vapor pressures reported by the Thermodynamic Research Center Data Project (*6*, *8*).

Booth and Swinehart (*1*) determined the vapor pressure from 9.20 atm to the critical at 49.62 atm. Owing to a typographical error, ref. *7* records the critical pressure as 46.62 atm. Stull (*9*), citing Booth and Swinehart, tabulates the vapor pressures from 1 to 760 mm Hg. The normal boiling point temperature is given as 241.15K (−32.0°C). These data must have been obtained by extrapolating the Booth and Swinehart data from 9.2 down to 1 atm and subsequently to 1 mm Hg. For a given vapor pressure, there is about a 5.5°C discrepancy between the data of Stull and that of Grosse et al. Ethyl fluoride vapor pressures reported in the "Chemical Engineers' Handbook" (*5*) are those of Stull.

Experimental

Vapor-pressure measurements were made on ethyl fluoride specially purified to 99.75 mol %. The major impurity was isobutane. Degassed ethyl fluoride was charged to chilled equilibrium cells that had been evacuated. Samples of the liquid and vapor phases in the equilibrium cell were analyzed for presence of heavies and light contaminants. Small traces of light contaminants were removed by boiling off some of the ethyl fluoride until the contaminants were undetectable.

Vapor-pressure measurements from 227.65 to 272.18K (data points 9–16) were taken in a high-precision cryogenic equilibrium cell. The thermostated vapor-sealed bath for the equilibrium cell was filled with methylcyclohexane. Temperature control at a predetermined level was achieved by balancing a constant liquid nitrogen cooling load against a 200-W heater controlled by a Precision Temperature Controller (Bayley Instrument Co.). Temperature measurement was by an L&N platinum resistance thermometer calibrated in terms of IPTS-68 and an L&N Mueller resistance thermometer bridge. Direct pressure measurements were by a calibrated 0–50 psia Heise gage. The uncalibrated Heise gage had an accuracy of 0.05 psia and a repeatability of 0.01 psia. The Heise gage was calibrated against a mercury manometer having an accuracy of 0.02 psia.

Vapor-pressure measurements from 273.54 to 322.48K were made in a Jurgeson gage equilibrium cell. The thermostated bath for this cell was filled with water. Temperature control was achieved by balancing a cooling fluid load against a Cole-Parmer temperature controller. Fluid circulating through the cooling coils was maintained at a constant temperature by an American Instrument Co. constant temperature bath. Temperature measurement was by a calibrated select thermocouple and an L&N potentiometer. Calibration was against ASTM precision thermometers having a maximum scale error of 0.2°F. Bath temperature was monitored by the ASTM precision thermometers. Pressure measurements of data points 17–29 were made by a calibrated 0–100 psia Heise gage. Data points 30–37 were measured by a 0–300 psia Heise gage maintained and calibrated at 125°F (325K). The 0–100 psia Heise gage had a repeatability of 0.02 psia and an accuracy of 0.1 psia. The uncalibrated 0–300 psia Heise gage had a repeatability of 0.06 psia and an accuracy of 0.3 psia. Both of these gages were calibrated against a Refinery Supply Co. dead weight gage having an accuracy of 0.1 psia.

Results

In this study the vapor pressures of ethyl fluoride were measured from 0.6893 to 16.77 atm and are recorded as data points 9–37 in Table I. The data of Grosse et al. (*4*) (0.01316–1.000 atm) are the first six data points of this table. The normal boiling points reported by Grosse (*2*) and Grosse and Linn (*3*) are represented by points 7 and 8. The high-pressure data of Booth and Swinehart (*1*) (19.20–49.62 atm) are recorded as data points 38–51.

A large ln P vs. T plot of all the data in Table I showed that the intermediate vapor-pressure measurements of this study blended in very well with literature values for both the low- (*2–4*) and the high-pressure (*1*) region. The normal boiling point reported by Grosse et al. and two of the points of Booth and Swinehart plotted slightly below a smooth curve drawn through all of the data. Stull's data (not presented in Table I) plotted uniformly and significantly below the curve.

A vapor-pressure equation obtained by regressing the present data alone to a four-parameter vapor-pressure equation predicted a normal boiling point of 235.44K (−37.71°C). All of the data in Table I were then regressed, resulting in an equation predicting the data to an average percent error of 0.61. An inspection of the deviation of the individual data points from the vapor-pressure equation showed that three of the data points could be considered as outliers. The data were re-regressed without these three data points. The resulting ethyl fluoride vapor-pressure equation is:

$$\ln P = 66.4460 - 3939.51/T + 0.0159614T - 9.79050 \ln T$$

Table I. Ethyl Fluoride Vapor Pressure

Data point	Temp, K	Press, atm	(Exp − calc) 100 / Exp
1	169.55	0.01316	+0.83
2	177.35	0.02632	−0.46
3	188.75	0.06579	−0.21
4	198.65	0.1316	−0.65
5	209.65	0.2632	−0.18
6[a]	236.05	1.000	−2.91
7	235.45	1.000	−0.15
8	235.45	1.000	−0.15
9	227.65	0.6893	−0.57
10	235.44	1.001	−0.01
11	244.12	1.465	+0.18
12	254.38	2.216	+0.40
13	254.83	2.259	+0.60
14	263.69	3.113	+0.05
15	270.43	3.953	+0.65
16	272.18	4.185	+0.51
17	273.54	4.389	+0.78
18	274.59	4.498	−0.20
19	274.62	4.538	+0.59
20	275.29	4.600	−0.23
21	275.50	4.634	−0.17
22	275.71	4.668	−0.12
23	276.13	4.736	−0.02
24	276.38	4.763	−0.26
25	278.12	5.076	+0.56
26	278.48	5.117	+0.22
27	278.61	5.137	+0.20
28	281.82	5.702	+0.62
29	287.48	6.756	+0.49
30	290.59	7.396	+0.45
31	292.32	7.784	+0.59
32	295.82	8.546	+0.52
33	302.26	10.19	+0.08
34	310.32	12.53	−0.20
35	317.26	14.87	−0.27
36	317.54	14.93	−0.55
37	322.48	16.77	−0.71
38	298.8	9.20	−0.80
39[a]	306.6	10.86	−5.10
40	316.7	14.58	+0.89
41[b]	324.8	17.74	−0.49
42	324.8	17.80	−0.15
43	333.79	21.92	+0.38
44	342.88	26.49	−0.15
45	351.73	31.79	−0.02
46	361.37	38.36	−0.03
47[a]	368.54	41.92	−4.68
48	374.14	48.87	+0.59
49	374.94	49.48	+0.40
50	375.12	49.49	+0.10
51[b]	375.31	49.62	+0.02

[a] Not used in regression. [b] Critical properties.

In this equation, T is in K and P is in atmospheres. This equation fit the combined experimental data to within an average error of 0.35% and a maximum error of 0.89%. The range of the regressed experimental vapor pressures covers about 3½ orders of magnitude (from 10 mm Hg to the critical at 49.62 atm). This equation predicts the normal boiling point of ethyl fluoride to be 235.42K (−37.73°C).

The three experimental points that were not used in obtaining the final correlation are noted in Table I. The criterion used for consideration of rejecting a data point from the final correlation was a comparison of the percent deviation of the data point from the correlating equation to the average percent deviation (0.35%). For the two data points of Booth and Swinehart (*1*) that were rejected, this ratio was 14.7 and 13.5. For the normal boiling point given by Grosse et al. (*4*), this ratio was 8.4. The ratio was 2.5 for the data point having the maximum deviation but still retained for the correlation.

Special consideration was given to the normal boiling point of Grosse et al. (*4*) before rejecting it from the final correlation. Under consideration was a normal boiling point of −37.7°C (refs. *2*, *3*, and present work) vs. −37.1°C (*4*).

In this article on physical properties of alkyl fluorides, no actual experimental data points are presented for ethyl fluoride. For ethyl fluoride the reported pressure-temperature values at fixed pressure levels were obtained in some manner from the experimental data.

In two earlier publications (*2*, *3*), the senior author reported the normal boiling point as −37.7°C.

The vapor-pressure equation reported in ref. *4* predicts a normal boiling point of −37.34°C. The reported vapor-pressure data were therefore not generated by an equation.

In ref. *4* experimental data are reported for *n*-propyl fluoride, as well as the tabulated data at fixed pressure levels and a vapor-pressure equation. For this component a ln P vs. $1/T$ interpolation of the experimental vapor-pressure data indicates a normal boiling point of −2.88°C; the reported vapor-pressure equation predicts −2.90°C. The normal boiling point, however, has been reported as −2.5°C. It is again not known how the tabulated data were generated from the experimental data.

The proposed ethyl fluoride vapor-pressure equation is in agreement with vapor pressures reported by the Thermodynamics Research Center Data Project (*6*, *8*). There is a slightly better agreement (maximum deviation 0.58% at 1500 mm Hg) with the 1956 (*6*) data than with the 1973 (*8*) revision (2.51% at 1500 mm Hg). This reflects a revision in the regressed normal boiling point from −37.7° (*6*) to −37.4°C (*8*). The data of Stull (*9*) as reported in the "Chemical Engineers' Handbook" (*5*) deviate from the proposed equation by an average greater than 30%.

Acknowledgment

This work was performed at Phillips Petroleum Co., and I am indebted to them for permission to publish these results.

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Received for review September 20, 1974. Accepted April 28, 1975.