Boiling Points and Boiling Point Numbers of Perfluoroalkanes and Perfluoroalkenes

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Application of the Kinney equation:

$$\text{b.p. in } ^\circ\text{C.} = 230.14(\text{total boiling point number})^{1/3} - 543$$

furnishes adequate results in calculations of normal boiling points of 75 aliphatic perfluorocarbons, including 23 linear and branched perfluoroalkanes, 22 perfluoroalkenes, and 30 perfluorocycloalkanes; the average error is 1.9°. This involves the use of seven new values of the boiling point number (b.p.n.); C, −1.83; F, 2.04; double bond, 4.27; also, four values for different rings.

SATISFACTORY results occur through application of the Kinney equation (*13–15*):

$$\text{b.p. in } ^\circ\text{C.} = 230.14(\text{total boiling point number})^{1/3} - 543 \quad (1)$$

in calculations of the normal boiling points of hydrocarbons (*13–15*), silanes and organosilicon compounds (*19*), germanes and alkylgermanium compounds (*1*), boranes and alkylboron compounds (*1*), alkyl derivatives of bivalent sulfur, selenium and tellurium (*1*), organic derivatives of trivalent phosphorus (*1*), and organic derivatives of trivalent arsenic (*1*).

Postelnek (*25*) fits the boiling points of 13 linear perfluoroalkanes adequately (average error, approximately 3.5°) with the equation:

$$\text{b.p. in } ^\circ\text{K.} = 540.87 \log(3 + \text{number of carbon atoms}) - 183.67 \quad (2)$$

Haszeldine and Smith (*12*) fit the boiling points of six linear perfluoroalkanes from n-C_7F_{16} to n-$C_{12}F_{26}$ adequately (average error, 0.7°) with the Lautié (*18*) equation:

$$(\text{b.p. in } ^\circ\text{K.})^2 = 15{,}400(\text{number of carbon atoms}) + 19{,}000 \quad (3)$$

However, this equation is unsatisfactory for calculations of boiling points below that of n-C_6F_{14}. They also fit four monocyclic perfluoroalkanes with a second (*12*) equation and two bicyclic perfluoroalkanes with a third equation.

Continued application of the Kinney equation, Equation 1, furnishes adequate results (average error, 1.9°) in calculations of normal boiling points of 13 linear perfluoroalkanes, 10 branched perfluoroalkanes, 22 perfluoroalkenes, and 30 perfluorocycloalkanes. This appears to be the first numerical treatment of perfluoroalkenes and branched perfluoroalkanes.

A mathematical study of the b.p.n. of the 14 linear perfluoroalkanes, C_nF_{2n+2}, in the first third of Table II shows the impossibility of obtaining a single accurate b.p.n. for the fluorine atom in both the CF_3 and the CF_2 groups while carbon has a positive b.p.n. In an earlier publication (*2*), a related method of calculation through the CF_2 increments in units of $(CF_2)_2$ allows evaluation of the C—F bond refraction as 1.84 ± 0.01 in organosilicon perfluoroesters, confirming the known C—F bond refraction of 1.850. Averaging all differences of $—CF_2CF_2—$ or larger in linear perfluoroalkanes furnishes 2.24 ± 0.11 for the b.p.n. of the CF_2 group. Next, subtraction of the portion of the total b.p.n. owing to the CF_2 groups and then division by 2 furnishes 4.28 ± 0.14 for the terminal CF_3 group. A random example, $CF_3CF_2CF_3$ yields $(10.60 - 2.24)/2 = 4.18$ per end CF_3 group. Now, the b.p.n. of 4.28 for end CF_3 and the b.p.n. of 2.24 for CF_2 indicate the b.p.n. of 2.04 for the fluorine atom and −1.84 for the carbon atom. However, later calculations on the compounds in Table II are based on the atomic b.p.n. of 2.04 for fluorine and −1.83 for carbon; this slight alteration better accomodates branched compounds, cyclics, and unsaturated compounds. Upon subtraction of the portion of each total b.p.n. owing to carbon and fluorine in 16 linear perfluoroalkenes and perfluoroalkadienes, the value of 4.27 ± 0.13 for the double bond results; this excludes $CF_2=CF_2$. Two cyclic perfluoroalkanes with three-membered rings similarly furnish 4.43 ± 0.07 for the b.p.n. of the probably strained three-membered ring. Fourteen cyclic perfluoroalkanes likewise furnish 3.87 ± 0.24 for the single ring with four carbon atoms or more. The b.p.n. of 7.59 ± 0.33 for the bicyclic ring or double ring fits data for 11 compounds. Also, the b.p.n. of 11.20 ± 0.11 for the tricyclic ring best fits the data for three tricyclic perfluorocycloalkanes.

In Table I, there are boiling point numbers for the carbon atom, the fluorine atom, the double bond, and four ring systems; there are five root mean square errors. In Table II, b.p. and b.p.n. for 75 compounds are calculated. This method does not include a calculated b.p. for CF_4.

LIMITATION

Table II excludes some compounds with normal b.p. at least 7° out of line with b.p. of closely related compounds, often because of difficulties in purification, in assignment of structure, or in accurate measurement of b.p. Exclusion from Table II is necessary for all linear perfluoroalkatrienes, for $CF_2=C=C=CF_2$ and similar compounds with double bonds on adjacent carbon atoms, and for two perfluoroalkynes.

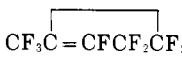
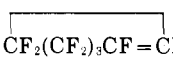
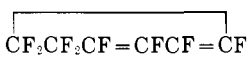
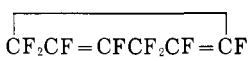
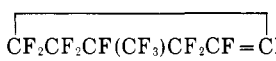
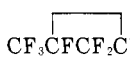
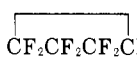
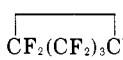
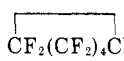
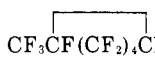
This method of calculation of b.p. does not fit the b.p. of CF_4 satisfactorily. Replacement of the constant, 543, in the Kinney equation by a new constant, 463, furnishes a new equation which fits the b.p. of CF_4 and the other linear and branched perfluoroalkanes quite well, but which fits the b.p. of perfluoroalkenes and perfluorocycloalkanes poorly.

Table I. Boiling Point Numbers of C, F, Rings, and Double Bond

Atom, Ring, or Double Bond	B.P.N.[a]
C	−1.83
F	2.04
C_3F_6 ring	4.43 ± 0.07
C_4F_8 ring or larger (monocyclic)	3.87 ± 0.24
Bicyclic or two rings separated	7.59 ± 0.33
Tricyclic ring	11.20 ± 0.11
Double bond	4.27 ± 0.13[b]

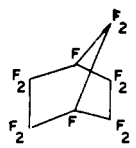
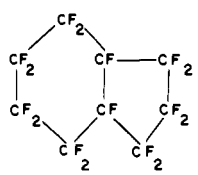
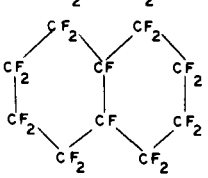
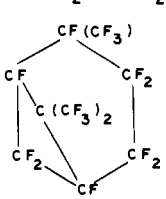
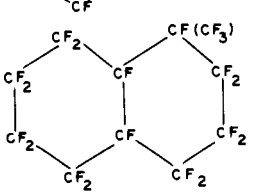
[a] B.p.n. with root mean square errors. [b] Excludes $CF_2=CF_2$ and compounds with double bonds on adjacent carbon atoms.

Table II. Calculations of Boiling Point

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., °C. Calcd.	B.P., °C. Found	Error	Ref.
CF_4	...	5.86	...	−128	...	(20)
C_2F_6	8.58	8.21	−71.8	−78.7	6.9	(20)
C_3F_8	10.83	10.60	−33.8	−37.5	3.7	(20)
n-C_4F_{10}	13.08	13.04	−0.7	−1.3	0.6	(3)
iso-C_4F_{10}	13.08	13.11	−0.7	−0.3	−0.4	(3)
n-C_5F_{12}	15.33	15.38	28.7	29.3	−0.6	(3)
$(CF_3)_2CFC_2F_5$	15.33	15.43	28.7	30.0	−1.3	(3)
$(CF_3)_4C$	15.33	15.44	28.7	30.1[a]	−1.4	(6)
n-C_6F_{14}	17.58	17.74	55.4	57.2	−1.8	(27)
$(CF_3)_2CFCF(CF_3)_2$	17.58	17.83	55.4	58.2	-2.8	(21)
$(CF_3)_2CF$-n-C_3F_7	17.58	17.78	55.4	57.7	−2.3	(27)
n-C_7F_{16}	19.83	20.06	79.9	82.3	−2.4	(8)
$C_3F_7CF(CF_3)C_2F_5$	19.83	19.98	79.9	81.5	−1.6	(10)
$(CF_3)_2CFC(CF_3)_3$	19.83	20.05	79.9	82.2	−2.3	(12)
n-C_8F_{18}	22.08	22.17	102.7	103.5	−0.8	(10)
$(C_2F_5)_2CF$-n-C_3F_7	22.08	22.12	102.7	103	−0.3	(26)
$(CF_3)_2CFCF_2C(CF_3)_3$	22.08	22.22	102.7	104	−1.3	(9)
n-C_9F_{20}	24.33	24.49	123.9	125.3	−1.4	(20)
n-$C_{10}F_{22}$	26.58	26.62	143.8	144.2	−0.4	(20)
$(CF_3)_2CF(CF_2)_4CF(CF_3)_2$	26.58	26.61	143.8	144.1	−0.3	(5)
n-$C_{11}F_{24}$	28.83	28.60	162.7	160.8	1.9	(20)
n-$C_{12}F_{26}$	31.08	30.76	180.6	178	2.6	(10)
n-$C_{13}F_{28}$	33.33	32.91	197.6	194.5	3.1	(20)
n-$C_{16}F_{34}$	40.08	39.23	244.6	239	5.6	(20)
$CF_3CF=CF_2$	11.02	11.11	−30.8	-29.4	−1.4	(20)
$CF_3CF_2CF=CF_2$	13.27	13.28	1.9	2.0	−0.1	(20)
$CF_3CF=CFCF_3$	13.27	13.13	1.9	1.0	0.9	(20)
$(CF_3)_2C=CF_2$	13.27	13.61	1.9	6.5	−4.6	(4)
$CF_3(CF_2)_2CF=CF_2$	15.52	15.39	31.1	29.5	1.6	(20)
$CF_3(CF_2)_3CF=CF_2$	17.77	17.72	57.6	57	0.6	(20)
$CF_3CF_2CF_2C(CF_3)=CF_2$	17.77	17.99	57.6	60	−2.4	(20)
$CF_3(CF_2)_4CF=CF_2$	20.02	19.93	81.9	81	0.9	(20)
$CF_3(CF_2)_5CF=CF_2$	22.27	22.32	104.5	105	−0.5	(20)
$CF_3(CF_2)_6CF=CF_2$	24.52	24.23	125.6	123	2.6	(20)
$CF_2=CFCF=CF_2$	13.46	13.69	4.5	7.5	−3.0	(20)
$CF_2=CFCF_2CF=CF_2$	15.71	15.86	33.4	35.2	−1.8	(22)
$CF_2=CF(CF_2)_2CF=CF_2$	17.96	17.95	59.7	59.6	0.1	(7)
$CF_2=CF(CF_2)_4CF=CF_2$	22.46	22.42	106.3	106	0.3	(17)
$CF_2=CF(CF_2)_6CF=CF_2$	26.96	27.07	147.1	148	−0.9	(16)
$CF_2=CF(CF_2)_8CF=CF_2$	31.46	31.20	183.5	181.5	2.0	(17)
	13.06	13.14	−1.0	0.1	−1.1	(23)
	15.31	14.95	28.5	24	4.5	(11)
	17.56	17.36	55.2	52.9	2.3	(20)
	17.75	17.74	57.3	57.2	0.1	(20)
	17.75	17.76	57.3	57.5	−0.2	(20)
	19.81	19.42	79.7	75.6	4.1	(20)
	11.18	11.11	−28.4	−29.5	1.1	(20)
	13.43	13.50	4.0	5.0	−1.0	(24)
	12.87	12.77	−3.7	−5	1.3	(20)
	15.12	14.92	26.1	23.6	2.5	(20)
	17.37	17.19	53.0	51	2.0	(20)
	19.62	19.46	77.7	76.0	1.7	(20)

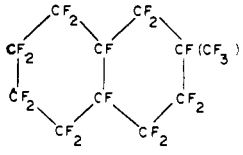
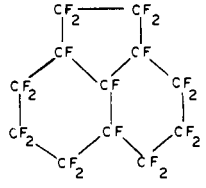
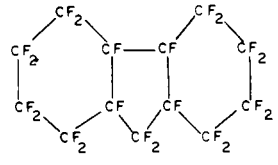
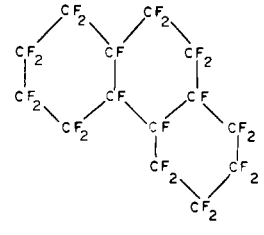
(*Continued on page 158*)

Table II. Calculations of Boiling Point (*Continued*)

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., °C. Calcd.	B.P., °C. Found	Error	Ref.
$(CF_3)_2C(CF_2)_3CF_2$	19.62	19.06	77.7	71.7	6.0	(*20*)
$C_2F_5CF(CF_2)_3CF_2$	19.62	19.36	77.7	75.0	2.7	(*20*)
$C_2F_5CF(CF_2)_4CF_2$	21.87	21.88	100.6	100.7	−0.1	(*20*)
$CF_3CFCF(CF_3)(CF_2)_3CF_2$	21.87	22.01	100.6	102.0	−1.4	(*20*)
$CF_3CFCF_2CF(CF_3)(CF_2)_2CF_2$	21.87	21.99	100.6	101.8	−1.2	(*20*)
$CF_2(CF_2)_6CF_2$	21.87	21.96	100.6	101.5	−0.9	(*20*)
$(CF_3)_2CFCF(CF_2)_4CF_2$	24.12	24.28	122.0	123.4	−1.4	(*20*)
$CF_3CFCF_2CF(CF_3)CF_2CF(CF_3)CF_2$	24.12	24.44	122.0	124.9	−2.9	(*20*)
$CF_3CFCF(CF_3)CF_2CF(CF_3)CF_2CF_2$	24.12	24.45	122.0	125	−3.0	(*20*)
$CF_3CF(CF_2)_4CFCF(CF_3)_2$	26.37	26.72	142.0	145	−3.0	(*20*)
$CF_2(CF_2)_4CFCF(CF_2)_4CF_2$	30.51	30.88	176.1	179	−2.9	(*20*)
$CF_2(CF_2)_4CFCF_2CF(CF_2)_4CF_2$	32.76	32.37	193.4	190.5	2.9	(*20*)
$CF_2(CF_2)_4CF(CF_2)_3CF(CF_2)_4CF_2$	37.26	37.23	225.7	225.5	0.2	(*20*)
$CF_2(CF_2)_4CF(CF_2)_4CF(CF_2)_4CF_2$	39.51	38.93	240.8	237	3.8	(*20*)
$CF_2(CF_2)_4CF(CF_2)_5CF(CF_2)_4CF_2$	41.76	41.92	255.5	256.5	−1.0	(*20*)
	19.26	18.95	73.9	70.6	3.3	(*20*)
	23.76	23.59	118.6	117.1	1.5	(*20*)
	26.01	26.25	138.9	141	−2.1	(*20*)
	26.01	26.09	138.9	139.6	−0.7	(*20*)
	28.26	28.63	158.0	161.1	−3.1	(*20*)

(*Continued on p. 159*)

Table II. Calculations of Boiling Point (*Continued*)

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., °C. Calcd.	B.P., °C. Found	B.P., °C. Error	Ref.
	28.26	28.62	158.0	161.0	−3.0	(*20*)
	30.04	30.16	172.4	173.4	−1.0	(*20*)
	32.29	32.31	189.9	190	−0.1	(*20*)
	34.54	34.40	206.5	205.5	1.0	(*20*)

[a] B.p. calculated from observed b.p. of 26° at 650 mm. pressure.

In the tables of a recent monograph (*20*), there are more than one thousand compounds containing carbon and fluorine; an excessive number of variables prevents easy discovery of regularities in the boiling points of most of these compounds. Usually at least one other element such as hydrogen is also present, which brings some association.

DISCUSSION OF RESULTS

Evaluation of the atomic b.p.n. of carbon and fluorine as −1.83 and 2.04, respectively, is the backbone of this paper; values of the b.p.n. of the double bond and the four ring systems are easy to derive after the b.p.n. of carbon and fluorine are known.

An average error of only 1.9° in the calculated boiling points in Table II demonstrates the reliability of the boiling point numbers in Table I.

Six perfluorocycloalkenes and perfluorocycloalkadienes in Table II have calculated boiling points that average 1.7° too high; the best explanation is that the value of the b.p.n. for the double bond (derived from the linear compounds) and the value of the monocyclic ring (derived from saturated compounds) are not quite additive in these six compounds.

Similarly, the values of the b.p.n. per ring in the cyclics are not quite additive for four-membered rings and larger: the b.p.n. per ring starts at 3.87 for monocyclics, then drops to 3.795 for the bicyclic or the double ring, and finally drops to 3.73 for the tricyclic ring.

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