di-(p-chlorophenyl)-disulfide, m.p. 70–71° (lit. (*6*), m.p. 70–71°).

Anal. Calcd. for $C_{12}H_8Cl_2S_2$: C, 50.02; H, 2.81; N, 0.0.

Found: C, 50.37; H, 3.02; N, <0.3.

The N-2,4-dinitrophenylmercaptoaziridines were not distilled, but were purified by recrystallization from ethanol.

Reaction of 1-(p-Chlorophenylmercopto)-arizidine with p-Chlorobenzenethiol. A solution of 1.108 grams of 1-(p-chlorophenylmercapto)-aziridine and 0.871 grams of p-chlorobenzenethiol in 20 ml. of benzene was allowed to stand for several hours at 30° C. Evaporation of the benzene and recrystallization of the residue from hexane gave 1.473 grams of S,S'-di-(p-chlorophenyl)-disulfide, m.p. 71–72°, undepressed on admixture with an authentic sample.

Reaction of 1-(p-Chlorophenylmercapto)-aziridine with Methyl Iodide. A solution of 1.0 grams of 1-(p-chlorophenylmercapto)-aziridine and 2.0 ml. of methyl iodide in 10 ml. of ethanol was allowed to stand at room temperature for several days. The solution became deep purple and a crystalline solid separated, which melted with decomposition at 236° C. and appeared to decompose on attempted recrystallization. The crude material was analyzed.

Anal Calcd. for $C_5H_{13}NI_2 + 0.3\ C_4H_{10}NI$: C, 18.58; H, 4.03; N, 4.55.

Found: C, 18.94; H, 4.05; N, 4.24.

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Boiling Points and Boiling Point Numbers of Perfluoroalkyl Compounds Containing Chlorine, Bromine, Iodine, Nitrogen, and Oxygen

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Application of the Kinney equation: b.p. in ° C. = 230.14(total boiling point number)$^{1/3}$ −543 and of the new equation: total boiling point number = $a + b$ (number of carbon atoms) $+ c$ furnishes satisfactory results (a simple average error of 1.2° and a maximum error of 4.4°) in calculations of normal boiling points of 175 compounds. These compounds include 108 perfluoroalkyl chlorides, bromides, and iodides and also 67 perfluoroalkyl compounds in 10 different series: acyl chlorides; primary, secondary, and tertiary amines; azomethines; diazo compounds; ethers; ketones; perfluoro (β-alkoxypropionic) acids; and nitro compounds. Thirty-five values for constants a, b, and c, including a value for the ring—and also seven atomic boiling point numbers for carbon and the four halogens in perfluoroalkyl chlorides, bromides, and iodides—are given.

ACCEPTABLE RESULTS occur in application of the Kinney equation (*34*):

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

in calculations of the normal boiling points of hydrocarbons (*34–36*), silanes and organosilicon compounds (*37*), boranes and alkylboron compounds (*1*), alkyl derivatives of bivalent sulfur, selenium, and tellurium (*1*), organic derivatives of trivalent phosphorus (*1*) and arsenic (*1*), perfluoroalkanes, perfluorocycloalkanes, and perfluoroalkenes (*1*), and some substituted perfluoralkanes. These substituted perfluoroalkanes include linear perfluoro monocarboxylic acids, perfluoro (β-alkoxypropionyl) fluorides, and also lone hydrogen, isocyanate, nitroso, perfluorooxacyclobutyl, sulfonyl fluoride, and the SF_4 or SF_5 groups (*1*).

Different methods (*23, 46*) are available for calculation of the normal boiling points of 6 or 13 linear perfluoroalkanes.

In the immediately previous publication on some substituted perfluoroalkanes (*1*), there is an adequate fit of 83 compounds in ten series with increments in boiling point number (b.p.n.) per CF_2 group in the range 2.22–2.29 through use of Equation 1 and the new general equation:

$$\text{total boiling point number} = -1.83A + 2.04B + Y \quad (2)$$

in which A is the number of carbon atoms in the perfluoroalkyl group or groups, B is the number of fluorine atoms attached to carbon, and Y is a substituted atom or group such as isocyanate.

Now, in turn, the present manuscript continues the study of substituted perfluoroalkanes in which the increments in b.p.n. per CF_2 group are outside the range 2.22–2.29 and thus not suited by Equation 2 above. Extensive data on the boiling points of perfluoroalkyl compounds containing chlorine, bromine, iodine, nitrogen, and oxygen offer ample ground for further study. As shown later, the development of suitable mathematical methods allows a very satisfactory fit between calculated normal boiling points and observed boiling points of 175 compounds of these types. Further equations related to Equation 2 are the backbone of the new methods.

Table I. Constants for Calculation of Total Boiling Point Numbers of Compounds Containing Nitrogen and Oxygen

total b.p.n. = $a + b$ (number of carbon atoms)

Homologous Series[a]	a	b	Root Mean Square Error,[b]	No.[c]
$R_fN{=}NR_f$	6.91	2.013[d]	1.85	5
$R_fN{=}CR_f'$ or $R_fCF_2N{=}CF_2$	6.50	1.897	0.93	7
R_fCOCl	6.66	2.347	2.00	7
$(R_f)_2NR_f'$	6.51	2.048	2.03	11
R_fNFR_f'	6.41	2.134	0.51	5
R_fNF_2	5.93	2.372	0.66	5
R_fCOR_f	4.97	2.062	1.10	6
$R_fOC_2F_4COOH$	16.66	1.856	2.00	8
R_fOR_f'	5.23	2.070	2.31	8
R_fNO_2	8.95	2.060	0.81	5

[a] R_f and R_f' are perfluoroalkyl groups such as CF_3, C_2F_5, $n\text{-}C_3F_7$ and larger; however, four compounds contain a branched group.

[b] Root mean square errors in calculations of boiling point in each series using these constants. See Table II.

[c] The number of compounds in each series—always at least five.

[d] Manual estimation of constants a and b by method of least squares; see last part of Discussion of Results.

Table II. Calculations of Boiling Point—Nitrogen and Oxygen Compounds

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., ° C. Calcd.	B.P., ° C. Found	B.P., ° C. Error	Ref.
$CF_3N{=}NCF_3$	10.94	10.95	−32.2	−32	−0.2	*(17)*
$CF_3N{=}NC_2F_5$	12.95	13.13	−2.6	0	−2.6	*(47)*
$C_2F_5N{=}NC_2F_5$	14.96	14.80	24.1	22	2.1	*(3)*
$n\text{-}C_3F_7N{=}N\text{-}n\text{-}C_3F_7$	18.99	18.80	71.0	69	2.0	*(3)*
$n\text{-}C_4F_9N{=}N\text{-}n\text{-}C_4F_9$	23.01	23.16	111.6	113	−1.4	*(11)*
$CF_3N{=}CFCF_3$	12.19	12.24	−13.3	−12.6	−0.7	*(13)*
$C_2F_5N{=}CF_2$	12.19	12.20	−13.3	−13.2	−0.1	*(45)*
$n\text{-}C_3F_7N{=}CF_2$	14.09	14.05	12.9	12.4	0.5	*(45)*
$CF_3N{=}CFC_2F_5$	14.09	14.12	12.9	13.2	−0.3	*(31)*
$C_2F_5N{=}CFCF_3$	14.09	14.08	12.9	12.8	0.1	*(31)*
$n\text{-}C_4F_9N{=}CF_2$	15.99	16.17	36.8	39	−2.2	*(45)*
$n\text{-}C_3F_7N{=}CFC_2F_5$	17.88	17.83	58.8	58.2	0.6	*(31)*
CF_3COCl	11.35	11.27	−25.8	−27	1.2	*(51)*
C_2F_5COCl	13.70	13.70	7.7	7.7	0.0	*(22, 30)*
$n\text{-}C_3F_7COCl$	16.05	16.19	37.5	39.2	−1.7	*(51)*
$n\text{-}C_4F_9COCl$	18.40	18.69	64.6	67.8	−3.2	*(51)*
$n\text{-}C_5F_{11}COCl$	20.74	20.40	89.3	85.9	3.4	*(51)*
$n\text{-}C_7F_{15}COCl$	25.44	25.34	133.9	133	0.9	*(27, 56)*
$n\text{-}C_9F_{19}COCl$	30.13	30.24	173.1	174	−0.9	*(15, 56)*
$(CF_3)_3N$	12.65	12.40	−6.7	−10.3	3.6	*(12, 33)*
$(CF_3)_2NC_2F_5$	14.70	14.68	20.8	20.5	0.3	*(12)*
$CF_3N(C_2F_5)_2$	16.75	16.76	45.8	46	−0.2	*(18, 33)*
$(C_2F_5)_3N$	18.80	18.80	69.0	69	0.0	*(18, 33)*
$(C_2F_5)_2N\text{-}n\text{-}C_3F_7$	20.85	21.10	90.4	93	−2.6	*(33)*
$(C_2F_5)_2N\text{-}n\text{-}C_4F_9$	22.89	23.23	110.5	113.7	−3.2	*(33)*
$C_2F_5(n\text{-}C_3F_7)_2$	22.89	23.08	110.5	112.3	−1.8	*(33)*
$C_2F_5N(iso\text{-}C_3F_7)_2$	22.89	22.63	110.5	108	2.5	*(43)*
$(n\text{-}C_3F_7)_3N$	24.94	25.01	129.8	130	−0.2	*(33)*
$(n\text{-}C_3F_7)_2N\text{-}iso\text{-}C_4F_9$	26.99	26.95	147.3	147	0.3	*(18)*
$(n\text{-}C_4F_9)_3N$	31.09	30.81	180.7	178.4	2.3	*(18, 33)*
$(CF_3)_2NF$	10.68	10.63	−36.2	−37	0.8	*(55)*
$CF_3NFC_2F_5$	12.81	12.86	−4.5	−3.8	−0.7	*(31)*
$(C_2F_5)_2NF$	14.95	14.95	23.9	23.9	0.0	*(31)*
$CF_3NF\text{-}n\text{-}C_3F_7$	14.95	14.98	23.9	24.3	−0.4	*(31)*
$(n\text{-}C_3F_7)_2NF$	19.21	19.19	73.4	73.2	0.2	*(31)*
CF_3NF_2	8.30	8.25	−77.3	−78	0.7	*(3)*
$C_2F_5NF_2$	10.67	10.69	−36.3	−36	−0.3	*(3)*
$n\text{-}C_3F_7NF_2$	13.05	13.13	−1.2	0	−1.2	*(3)*
$n\text{-}C_4F_9NF_2$	15.42	15.39	29.8	29.5	0.3	*(7)*
$n\text{-}C_5F_{11}NF_2$	17.79	17.76	57.8	57.5	0.3	*(7)*
CF_3COCF_3	11.16	11.21	−28.7	−28	−0.7	*(16)*
$C_2F_5COCF_3$	13.22	13.12	1.2	−0.2	1.4	*(29)*
$n\text{-}C_3F_7COCF_3$	15.28	15.42	28.1	29.8	−1.7	*(18)*
$C_2F_5COC_2F_5$	15.28	15.19	28.1	27	1.1	*(57)*
$n\text{-}C_3F_7COC_2F_5$	17.34	17.28	52.7	52	0.7	*(18)*
$n\text{-}C_3F_7CO\text{-}n\text{-}C_3F_7$	19.41	19.44	75.5	75.8	−0.3	*(57)*

Table II. Calculations of Boiling Point—Nitrogen and Oxygen Compounds (Continued)

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., ° C. Calcd.	B.P., ° C. Found	B.P., ° C. Error	Ref.
$CF_3OC_2F_4COOH$	24.08	24.56	121.6	126	−4.4	*(8)*
$C_2F_5OC_2F_4COOH$	25.94	25.68	138.3	136	2.3	*(8)*
n-$C_3F_7OC_2F_4COOH$	27.80	27.54	154.2	152	2.2	*(8)*
n-$C_4F_9OC_2F_4COOH$	29.65	29.49	169.3	168	1.3	*(8)*
n-$C_5F_{11}OC_2F_4COOH$	31.51	31.52	183.9	184	−0.1	*(8)*
n-$C_6F_{13}OC_2F_4COOH$	33.36	33.38	197.9	198	−0.1	*(8)*
n-$C_7F_{15}OC_2F_4COOH$	35.22	35.31	211.4	212	−0.6	*(8)*
n-$C_8F_{17}OC_2F_4COOH$	37.08	37.16	224.4	225	−0.6	*(8)*
CF_3OCF_3	9.37	9.30	−57.8	−59	1.2	*(50)*
$C_2F_5OC_2F_5$	13.51	13.21	5.1	1	4.1	*(50)*
n-$C_4F_9OCF_3$	15.58	15.92	31.8	36.0	−4.2	*(50)*
n-C_3F_7O-n-C_3F_7	17.65	17.63	56.2	56	0.2	*(50)*
n-C_4F_9O-n-C_4F_9	21.79	21.97	99.8	101.6	−1.8	*(50)*
CF_3O-n-C_7F_{15}	21.79	21.80	99.8	100	−0.2	*(32)*
n-$C_5F_{11}O$-n-C_5F_{11}	25.93	25.98	138.2	138.6	−0.4	*(50)*
CF_3O-n-$C_{10}F_{21}$	28.00	27.78	155.8	154	1.8	*(32)*
CF_3NO_2	11.01	11.00	−31.0	−31.1	0.1	*(21)*
$C_2F_5NO_2$	13.07	13.10	−0.9	−0.5	−0.4	*(18)*
n-$C_3F_7NO_2$	15.13	15.03	26.2	25	1.2	*(18)*
iso-$C_3F_7NO_2$	15.13	15.23	26.2	27.5	−1.3	*(2)*
$(CF_3)_3CNO_2$	17.19	17.19	51.0	51	0.0	*(2)*

Table III. Constants to Calculate Total Boiling Point Numbers of Compounds Containing Chlorine, Bromine, and Iodine—Atomic B.P.N.s

total b.p.n. = $a + b$ (number of carbon atoms) $+ c$

Homologous Series or Ring	a	b	c	R.M.S. Error in B. P., °C.	No.	Atomic B.P.N.s		
						C	F	Cl, Br, or I
R_fCl[a]	5.81[b]	2.403	0	1.2[c]	10[d]	−1.955	2.179	3.63
$C_nCl_2F_{2n}$			2.86 ± 0.12	1.2	14			4.335
$C_nCl_3F_{2n-1}$			6.12 ± 0.11	1.1	11			4.703
$C_nCl_4F_{2n-2}$			10.14 ± 0.16	1.5	13			5.077
$C_nCl_5F_{2n-3}$			14.66 ± 0.17	1.3	9			5.403
$C_nCl_6F_{2n-4}$			19.67 ± 0.29	2.1	6			5.699
R_fBr	6.67	2.506	0	1.4	7	−2.038	2.272	4.40
$C_nBr_2F_{2n}$			4.90 ± 0.15	1.5	7			5.785
$C_nBr_3F_{2n-1}$			11.35 ± 0.14	1.2	2			6.765
$C_nBr_4F_{2n-2}$			20.07 ± 0.10	0.8	2			7.821
R_fI	9.10	2.424	0	1.2	10	−1.9715	2.1977	6.902
Ring, 4–6[e] membered	. . .	. . .	3.81 ± 0.17	1.6	17	. . .	. . .	. . .

[a] R_f is a linear perfluoroalkyl group such as CF_3 or larger; n is two or more. [b] Manual estimation of constants a and b by method of least squares. [c] Root mean square error in calculations of normal boiling point in each series upon addition of appropriate constant c to calculated b.p.n. of corresponding R_fCl, R_fBr, or R_fI in Table II, or upon use of constants a, b and c. [d] The number of compounds in each series. [e] Add 3.81 for the ring to appropriate sum of $a + b$(number of carbon atoms) $+ c$; subtract b.p.n. for two fluorine atoms as follows: bromides, 4.54; chlorides, 4.36; iodides, 4.40.

In calculations of boiling points of 67 perfluoroalkyl compounds containing nitrogen and oxygen, Equation 1 and ten individual equations of the general type:

$$\text{total boiling point number} = a + b\,(\text{number of carbon atoms}) \qquad (3)$$

are used with all solutions by the method of least squares. In Table I there are twenty values of constants a and b in Equation 3; also, there are root mean square errors in calculations of boiling points in the ten series, and the number of compounds (always at least five) in each of the series. In Table II there are calculated normal boiling points for 67 compounds containing perfluoroalkyl groups and nitrogen or oxygen; the mathematical method consists of first finding the total boiling point number of the individual compound according to Equation 3, and then finding the calculated boiling point of the compound according to Equation 1.

Attempted use of logarithmic equations (*46*) furnishes a less satisfactory fit for the 67 compounds containing nitrogen and oxygen than the above method relying on Equations 1 and 3.

Calculations of the normal boiling points of 108 perfluoroalkyl chlorides, bromides, and iodides involve use of Equation 1 and the new equation:

$$\text{total boiling point number} = a + b\,(\text{number of carbon atoms}) + c \qquad (4)$$

in which each series such as linear perfluoroalkyl chlorides has its own value of a and b. The manual mathematical procedures follow in chronological order. First, there is a least-squares solution for constants a and b in each of the three homologous series R_fCl, R_fBr, and R_fI, using carefully selected or averaged normal boiling points. These six constants are in Table III; constant c is zero in these three series. Second, after indication that the atomic b.p.n. of chlorine is variable when two to six chlorine atoms are in the molecule, there is calculation of five different values of constant c for chlorine in Equation 4. For example, take the random example $CClF_2CClFCClF_2$, one of four isomers of $C_3Cl_3F_5$ in Table IV; subtraction of 13.02, the calculated b.p.n. of $CClF_2CF_2CF_3$ (the corresponding R_fCl), from the observed total b.p.n. of 19.24 furnishes 6.22 for con-

Table IV. Calculations of Boiling Point of Compounds Containing Chlorine, Bromine, and Iodine

	B.P.N.		B.P., ° C.			
Compound	Calcd.	Found	Calcd.	Found	Error	Ref.
$CClF_3$	8.21	8.09	−78.7	−81	2.3	*(10, 18)*
$CClF_2CF_3$	10.62	10.58	−37.1	−37.7	0.6	*(5, 10, 26)*
$CClF_2CF_2CF_3$	13.02	13.02	−1.6	−1.6	0.0	*(6, 18, 26, 52)*
$CClF_2(CF_2)_2CF_3$	15.42	15.42	29.8	29.8	0.0	*(6, 18)*
$CClF_2(CF_2)_3CF_3$	17.83	17.94	58.2	59.5	−1.3	*(6, 18)*
$CClF_2(CF_2)_4CF_3$	20.23	20.39	84.1	85.8	−1.7	*(6, 18)*
$CClF_2(CF_2)_5CF_3$	22.63	22.79	108.0	109.5	−1.5	*(18)*
$CClF_2(CF_2)_6CF_3$	25.03	24.95	130.2	129.5	0.7	*(49)*
$CClF_2(CF_2)_7CF_3$	27.44	27.36	151.2	150.5	0.7	*(6)*
$CClF_2(CF_2)_8CF_3$	29.84	29.74	170.8	170	0.8	*(6)*
$CBrF_3$	9.18	9.30	−61.1	−59	−2.1	*(9, 18)*
$CBrF_2CF_3$	11.68	11.67	−20.8	−21	0.2	*(26)*
$CBrF_2CF_2CF_3$	14.19	14.02	14.2	12	2.2	*(18, 26)*
$CBrF_2(CF_2)_2CF_3$	16.69	16.57	45.1	43.8	1.3	*(18)*
$CBrF_2(CF_2)_3CF_3$	19.20	19.29	73.3	74.2	−0.9	*(18, 26)*
$CBrF_2(CF_2)_4CF_3$	21.71	21.83	99.0	100.2	−1.2	*(18)*
$CBrF_2(CF_2)_5CF_3$	24.21	24.18	122.8	122.5	0.3	*(49)*
CF_3I	11.52	11.57	−23.2	−22.5	−0.7	*(4, 24)*
CF_3CF_2I	13.95	14.08	11.0	12.8	−1.8	*(4, 24)*
$CF_3CF_2CF_2I$	16.37	16.36	41.4	41.2	0.2	*(24)*
$CF_3(CF_2)_2CF_2I$	18.80	18.62	69.0	67	2.0	*(18)*
$CF_3(CF_2)_3CF_2I$	21.22	21.24	94.2	94.4	−0.2	*(25)*
$CF_3(CF_2)_4CF_2I$	23.64	23.58	117.5	117	0.5	*(18)*
$CF_3(CF_2)_5CF_2I$	26.07	25.85	139.4	137.5	1.9	*(18)*
$CF_3(CF_2)_6CF_2I$	28.49	28.56	159.9	160.5	−0.6	*(18)*
$CF_3(CF_2)_7CF_2I$	30.92	31.13	179.3	181	−1.7	*(18)*
$CF_3(CF_2)_8CF_2I$	33.34	33.31	197.7	197.5	0.2	*(18)*
$CClF_2CClF_2$	13.48	13.40	4.7	3.7	1.0	*(38)*
CF_3CCl_2F	13.48	13.40	4.7	3.6	1.1	*(38)*
$CClF_2CCl_2F$	16.74	16.85	45.7	47.0	−1.3	*(38)*
CF_3CCl_3	16.74	16.76	45.7	46.0	−0.3	*(38)*
$CClF_2CCl_3$	20.76	20.96	89.5	91.5	−2.0	*(38)*
CCl_2FCCl_2F	20.76	21.07	89.5	92.7	−3.2	*(38)*
$CF_3CF_2CCl_2F$	15.88	15.84	35.5	35	0.5	*(38)*
$CF_3CClFCClF_2$	15.88	15.81	35.5	34.6	0.9	*(38)*
$CF_3CCl_2CF_3$	15.88	15.67	35.5	32.9	2.6	*(39)*
$CClF_2CF_2CClF_2$	15.88	15.90	35.5	35.7	−0.2	*(38)*
$CF_3CF_2CCl_3$	19.14	18.94	72.6	70.5	2.1	*(38)*
$CF_3CClFCCl_2F$	19.14	19.22	72.6	73.5	−0.9	*(38)*
$CF_3CCl_2CClF_2$	19.14	19.08	72.6	72	0.6	*(38)*
$CClF_2CClFCClF_2$	19.14	19.24	72.6	73.7	−1.1	*(38)*
$CF_3CClFCCl_3$	23.16	23.11	113.0	112.5	0.5	*(38)*
$CF_3CCl_2CCl_2F$	23.16	23.16	113.0	113	0.0	*(38)*
$CClF_2CF_2CCl_3$	23.16	23.29	113.0	114.2	−1.2	*(38)*
$CClF_2CClFCCl_2F$	23.16	23.07	113.0	112.2	0.8	*(38)*
$CClF_2CCl_2CClF_2$	23.16	23.05	113.0	112	1.0	*(38)*
$CCl_2FCF_2CCl_2F$	23.16	23.23	113.0	113.7	−0.7	*(38)*
$CF_3CCl_2CCl_3$	27.68	27.60	153.2	152.5	0.7	*(38)*
$CClF_2CClFCCl_3$	27.68	27.69	153.2	153.3	−0.1	*(38)*
$CCl_2FCF_2CCl_3$	27.68	27.84	153.2	154.5	−1.3	*(38)*
$CClF_2CCl_2CCl_2F$	27.68	27.57	153.2	152.3	0.9	*(38)*
$CCl_2FCClFCCl_2F$	27.68	27.86	153.2	154.7	−1.5	*(38)*
$CCl_2FCClFCCl_3$	32.69	33.11	192.9	196	−3.1	*(38)*
$CCl_2FCCl_2CCl_2F$	32.69	32.87	192.9	194.2	−1.3	*(38)*
$CCl_3CF_2CCl_3$	32.69	32.89	192.9	194.4	−1.5	*(38)*
$CF_3CF_2CF_2CCl_2F$	18.28	18.24	63.3	62.8	0.5	*(38)*
$CF_3CF_2CCl_2CF_3$	18.28	18.35	63.3	64	−0.7	*(38)*
$CF_3CClFCClFCF_3$	18.28	18.25	63.3	62.9	0.4	*(28)*
$CF_3CCl(CF_3)CClF_2$	18.28	18.26	63.3	63	0.3	*(38)*
$CClF_2CF_2CF_2CClF_2$	18.28	18.35	63.3	64	−0.7	*(40)*
$CF_3CF_2CF_2CCl_3$	21.54	21.43	97.3	96.3	1.0	*(38)*
$CF_3CClFCCl_2CF_3$	21.54	21.56	97.3	97.5	−0.2	*(38)*
$CClF_2CClFCF_2CClF_2$	21.54	21.61	97.3	98	−0.7	*(38)*
$CClF_2CClFCClFCClF_2$	25.56	25.34	134.9	133	1.9	*(38)*
$CClF_2CF_2CCl_2CClF_2$	25.56	25.48	134.9	134.2	0.7	*(38)*
$CClF_2CClFCF_2CCl_2F$	25.56	25.40	134.9	133.5	1.4	*(38)*
$CF_3CCl_2CCl_2CF_3$	25.56	25.40	134.9	133.5	1.4	*(38)*
$CF_3CCl_2CF_2CCl_3$	30.08	29.80	172.7	170.5	2.2	*(38)*
$CClF_2CCl_2CF_2CCl_2F$	30.08	29.90	172.7	171.3	1.4	*(38)*
$CClF_2CClFCCl_2CClF_2$	30.08	30.11	172.7	173	−0.3	*(20)*
$CClF_2CClFCClFCCl_2F$	30.08	30.36	172.7	175	−2.3	*(20)*
$CCl_3CF_2CF_2CCl_3$	35.09	34.89	210.5	209	1.5	*(38)*
$CCl_2FCClFCClFCCl_2F$	35.09	34.68	210.5	207.5	3.0	*(38)*

Table IV. Calculations of Boiling Point of Compounds Containing Chlorine, Bromine, and Iodine (Continued)

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., ° C. Calcd.	B.P., ° C. Found	Error	Ref.
$CCl_3CF_2CCl_2CClF_2$	35.09	34.89	210.5	209	1.5	(*38*)
$CF_3CF_2CClFCF_2CCl_2F$	23.95	23.80	120.4	119	1.4	(*38*)
$C_2F_5CClFCClFC_2F_5$	23.09	22.95	112.4	111	1.4	(*38*)
$CClF_2(CF_2)_4CClF_2$	23.09	23.32	112.4	114.5	−2.1	(*38*)
$CF_3CF_2CF(CF_3)CClFCClF_2$	23.09	23.32	112.4	114.5	−2.1	(*42*)
$CF_3(CF_2)_4CCl_3$	26.35	26.48	141.9	143	−1.1	(*38*)
$CF_3CClFCCl(CF_3)CClFCClF_2$	30.37	30.59	175.1	176.8	−1.7	(*41*)
$CBrF_2CBrF_2$	16.59	16.80	44.0	46.4	−2.4	(*38*)
$CF_3CBrFCBrF_2$	19.09	19.01	72.1	71.2	0.9	(*9*)
$CBrF_2CF_2CBrF_2$	19.09	19.29	72.1	74.2	−2.1	(*38*)
$CBrF_2(CF_2)_2CBrF_2$	21.59	21.60	97.8	97.9	−0.1	(*38*)
$C_2F_5CBrFCBrF_2$	21.59	21.39	97.8	95.9	1.9	(*38*)
$CF_3CBr(CF_3)CBrF_2$	21.59	21.49	97.8	96.9	0.9	(*38*)
$CF_3CBrFCBrFCF_3$	21.59	21.49	97.8	96.9	0.9	(*38*)
CF_3CBr_3	23.03	23.17	111.8	113.1	−1.3	(*38*)
$CBrF_2CBrFCBrF_2$	25.54	25.41	134.8	133.6	1.2	(*14*)
CBr_2FCBr_2F	31.75	31.86	185.8	186.6	−0.8	(*38*)
$CBrF_2CBr_3$	31.75	31.65	185.8	185	0.8	(*38*)
$CF_2CClFCF_2CClF$	17.73	17.90	57.1	59.0	−1.9	(*38*)
$CF_2CF_2CClFCCl_2$	20.99	21.25	91.9	94.5	−2.6	(*38*)
$CF_2CF_2CCl_2CCl_2$	25.01	25.15	130.0	131.3	−1.3	(*38*)
$CF_2CCl_2CF_2CCl_2$	25.01	24.84	130.0	128.5	1.5	(*38*)
$CClFCClFCClFCClF$	25.01	24.90	130.0	129	1.0	(*38*)
$CClFCCl(CF_3)CF_2CF_2$	20.14	19.84	83.2	80	3.2	(*19*)
$CClFCClF(CF_2)_3CF_2$	22.54	22.74	107.1	109	−1.9	(*48, 54*)
$CClF(CF_2)_4CFCF_3$	22.08	22.12	102.7	103	−0.3	(*19*)
$CClFCClF(CF_2)_3CFCF_3$	24.94	25.01	129.4	130	−0.6	(*38*)
$CF_2(CF_2)_4CBrF$	20.98	20.85	91.8	90.4	1.4	(*38*)
$CBrFCBrF(CF_2)_3CF_2$	25.88	26.12	137.7	139.8	−2.1	(*19*)
$CBrF(CF_2)_4CFCF_3$	23.48	23.44	116.0	115.6	0.4	(*38*)
$CBrFCBrF(CF_2)_3CFCF_3$	28.38	28.50	159.0	160	−1.0	(*38*)
$CF_2(CF_2)_2CFI$	18.21	18.26	62.5	63	−0.5	(*38*)
$CF_2CF_2CFICFCF_3$	20.62	20.41	88.1	86	2.1	(*38*)
$CF_2(CF_2)_4CFI$	23.05	23.05	112.0	112	0.0	(*38*)
$CF_2(CF_2)_3CFICFCF_3$	25.48	25.23	134.2	132	2.2	(*19*)

stant c—the average value 6.12 for constant c appears in Table III. Add constant c to the calculated b.p.n. of the corresponding R_fCl to obtain the calculated b.p.n. of any isomer of $C_nCl_3F_{2n-1}$; root mean square errors for each value of the constant c are in Table III. Similar calculations based on calculated b.p.n.s. of the corresponding R_fBr compounds yield three values for constant c. Third, there is calculation of the portion of the total b.p.n. attributable to the 4-membered, 5-membered, or 6-membered rings present in 17 compounds in Table IV. For a random example, take cyclo-$C_7Br_2F_{12}$ fifth from the end in Table IV; from the observed total b.p.n. of 28.50 subtract 24.21, the calculated total b.p.n. of n-C_7BrF_{15}, and 4.90, the increment from R_fBr to $C_nBr_2F_{2n}$ (one value of constant c), but add 4.54 for two fluorine atoms to obtain 3.93 for the b.p.n. of the ring. Estimation of the atomic b.p.n. of fluorine depends on the assumption that its value is proportionately larger than the b.p.n. for fluorine in perfluoroalkanes (*1*) according to the equation:

$$\text{atomic b.p.n. of fluorine} = 2.04(2.403/2.25) \qquad (5)$$

which furnishes 2.179 for the fluorine atom in R_fCl and derivatives of it. Here 2.403 is the increment in b.p.n. per CF_2 group in R_fCl (constant b in Table III) and 2.25 is the CF_2 increment in perfluoroalkanes (*1*). Similarly the atomic b.p.n. of carbon in R_fCl comes out −1.955; related calculations give atomic b.p.n.s. for carbon and fluorine in R_fBr and R_fI. Fourth, there is estimation of the atomic b.p.n.s of chlorine, bromine, and iodine based on constants in Table III. Subtraction of 2.179 for one fluorine atom from 5.81—constant a for R_fCl obtained by subtraction of 2.403 from 8.21, the calculated b.p.n. of $CClF_3$—leaves 3.63 as the atomic b.p.n. of chlorine in this configuration. To obtain the atomic b.p.n. of chlorine in $C_nCl_2F_{2n}$ add 3.63, chlorine in R_fCl, 2.86, the increment from R_fCl to $C_nCl_2F_{2n}$, and 2.18, fluorine in R_fCl; divide the resulting 8.67 by 2 and obtain 4.335 for this atomic b.p.n. of chlorine. An alternate method, with occasional slight loss in accuracy, is to select from Table IV a calculated total b.p.n. such as that for the two isomers of $C_2Cl_2F_4$, 13.48; subtract 8.716 for four fluorine atoms and −3.910 for two carbon atoms to obtain 8.674, which upon division by 2 furnishes 4.337 for this chlorine. Comparable procedures give the other atomic b.p.n.s in Table III. Fifth, there is calculation of 108 normal boiling points in Table IV.

As explained in the immediately previous publication (*1*), there is minor correction of observed boiling points under slightly different pressures to normal boiling points under 760 mm. via Myers' equation (*44*).

LIMITATION

Table II excludes some compounds with a normal b.p. more than 5° out of line with b.p.s of compounds in the same series—such as $CF_3N{=}CF_2$, $(n\text{-}C_5F_{11})_3N$, *iso*-C_3F_7CO-*iso*-C_3F_7 (*53*), *n*-$C_6F_{13}O$-*n*C_6F_{13} (*50*) and CF_3O-*n*$C_{13}F_{27}$ (*32*). Only four compounds with a branched perfluoroalkyl group appear in Table II; the calculations are the same as those for the corresponding linear compounds. No perfluoroalkyl diketones (*53*) are in Table II. A requirement of at least five compounds in each series excludes some types listed in a recent monograph (*38*).

Table IV excludes all compounds such as CCl_2F_2, CCl_3F, CBr_2F_2, and CBr_3F—which would result if n in the formulas in Table III took the unacceptable value of one—and also excludes a few compounds like CF_3CFXCF_3 in which X is chlorine, bromine, or iodine.

DISCUSSION OF RESULTS

Calculation of 175 normal boiling points via Equation 1 and either Equation 3 or Equation 4 involves a simple average error of only 1.2°, a maximum error of 4.4°, and an over-all root mean square error of 1.5°. Other publications in this series (*1*) involve larger errors.

All isomers of any one compound have the same calculated total b.p.n. and calculated normal boiling point herein.

Atomic b.p.n.s for carbon and the four halogens in the various configurations also allow calculation of total b.p.n.s and normal boiling points of perfluoroalkyl chlorides, bromides, and iodides. A relatively more rapid rise in the atomic b.p.n.s of bromine rather than chlorine is consistent with the greater polarizability of bromine, and with the bond energies, in kcal.: C—F, 107; C—Cl, 78; C—Br, 65.3.

The calculated b.p.n. of the ring herein, 3.81, is close to the previous value of 3.87 for the monocyclic C_4F_8 ring or larger (*1*).

In the perfluoroalkyl compounds containing nitrogen and oxygen, the final constant a is without presence of any carbon atoms. For a random example, take the perfluoroacyl chlorides; mathematical solution via least squares furnishes the calculated total b.p.n. of 11.356 for CF_3COCl, the first member of the series. Upon subtraction of 4.694 for two CF_2 groups. this furnishes 6.66 for the conveniently adjusted constant a in Equation 3. It is best not to combine the three classes of perfluoroalkyl amines into a single series; in each of these three series the constant a corresponds to, but does not exactly equal, the observed b.p.n. for NF_3, 6.25.

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