δ = a very small correction term, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer, to take account of the variations in mass of the glass ampoule from the standard value, and variations in the mean temperature of an experiment from the standard value of 29° C.

The mean value of the energy equivalent, E_i, is for an initial system containing a benzoic acid pellet having a mass equal to the mean of the masses of the pellets used in the experiments. However, the desired energy equivalent for the alcohol experiments is that for a system containing no pellet, but containing instead a mass of soft glass equal to the mean mass of the glass ampoules used in the alcohol experiments. The following expressions were used in calculating the desired energy equivalent, E_{si}:

$$E_{si} = E_i - D(1.21\, m_s - 0.711\, m_g)$$

Here,

D = number of degrees Celsius (centigrade) equivalent to one unit of the temperature scale used

m_s = the mean mass, in grams, of the pellets of benzoic acid used in the calibration experiments

m_g = the mean mass in grams, of the soft glass ampoules used in the experiments

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Boiling Points and Boiling Point Numbers of Some Substituted Perfluoroalkanes

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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 (root mean square error, 2.6°; simple average error, 2.0°) in calculations of normal boiling points of 83 substituted perfluoroalkanes. These include straight chain perfluoromonocarboxylic acids, perfluoro(β-alkoxypropionyl) fluorides, and perfluoroalkyl compounds containing isocyanate, nitroso, perfluorooxacyclobutyl, lone hydrogen, sulfonyl fluoride, the SF_4 group, and the SF_5 group. Calculations involve use of 10 new values of the boiling point number (b.p.n.) and the previous b.p.n.s. of −1.83 for carbon and 2.04 for fluorine in perfluoroalkanes.

ACCEPTABLE results occur in application of the Kinney equation (*17–19*):

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

in calculations of the normal boiling points of hydrocarbons (*17–19*), silanes and organosilicon compounds (*21*), germanes and alkylgermanium compounds (*3*), boranes and alkylboron compounds (*3*), alkyl derivatives of bivalent sulfur, selenium, and tellurium (*3*), alkyl derivatives of trivalent organophosphorus compounds (*3*), alkyl derivatives of trivalent organoarsenic compounds (*3*), and perfluoroalkanes, perfluorocycloalkanes and perfluoroalkenes (*3*).

Postelnek (*24*) and Haszeldine and Smith (*14*) offer other methods of calculation on boiling points of saturated linear perfluoroalkanes and a few cycloperfluoroalkanes.

Satisfactory calculations of b.p.n.s through the Kinney equation (*17*) (Equation 1) are practical in 10 homologous series of substituted perfluoroalkanes in which the average increment in b.p.n. per CF_2 group varies only between 2.22 and 2.29. Calculations in each series involve all possible mathematical combinations. Published (*3*) atomic b.p.n.s of −1.83 for carbon and 2.04 for fluorine furnish the b.p.n. 2.25 for CF_2 and fit these 10 series adequately (while there is omission of 12 series with increments in b.p.n. per CF_2 group in the ranges 1.85 to 2.14 and 2.34 to 2.50). Further

Table I. Boiling Point Numbers of Atoms and Groups[a]

Atom or Group	B.P.N.
NCO	6.38 ± 0.23[b]
NO	3.67 ± 0.18
(O + ring) in perfluorooxacyclobutane[c]	3.75 ± 0.26
Primary lone hydrogen, as in R_fCF_2H[d]	3.45 ± 0.33
Secondary or tertiary lone hydrogen, as in R_fR_f' CFH or $(R_f)_3CH$[d]	2.95 ± 0.07
COOH, in straight chain R_fCOOH[d]	14.93 ± 0.16
(O + CO) in $R_fOCF_2CF_2COF$[d]	2.78 ± 0.31
SO_2F in R_fSO_2F[d]	7.48 ± 0.25
SF_5 in R_fSF_5[d]	7.83 ± 0.24
SF_4 in $R_fSF_4R_f'$[d]	5.99 ± 0.15

[a] Perfluoroalkyl C, −1.83; F, 2.04 (to C); ring 3.87 (secondary lone hydrogen only). [b] Root mean square errors. [c] Perfluorooxacyclobutane is $\overbrace{CF_2CF_2CF_2}^{O}$. [d] R_f and R_f' are perfluoroalkyl groups.

progress occurs through use of the new general equation:

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

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 one of 10 substituted atoms or groups such as isocyanate. For a random example of the use of Equation 2, solve for the b.p.n. of NCO in the compound C_2F_5NCO according to the specific equation:

$$12.88 = -1.83 \times 2 + 2.04 \times 5 + Y \qquad (3)$$

and find 6.34 for Y, the b.p.n. of NCO in this compound.

Sometimes, it is necessary to correct boiling points at the observed pressure P, in millimeters of mercury (usually above 700 mm.), to normal b.p.s at 760 mm. using the equation (*23*):

$$\Delta T = 0.00012(273 + T)\ (760 - P) \qquad (4)$$

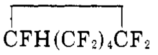
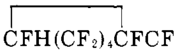
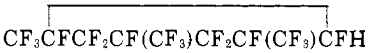
in which T is the observed b.p. in ° C. Thus the normal b.p.,

Table II. Calculations of Boiling Point

	B.P.N.		B.P., ° C.			
Compound	Calcd.	Found	Calcd.	Found	Error	Ref.
CF_3NCO	10.67	10.69	−36.3	−36	−0.3	(*4*)
C_2F_5NCO	12.92	12.88	−3.0	−3.5	0.5	(*9*)
n-C_3F_7NCO	15.17	15.08	26.7	25.6	1.1	(*1*)
n-C_4F_9NCO	17.42	17.44	53.6	53.8	−0.2	(*1*)
n-$C_5F_{11}NCO$	19.67	19.63	78.4	77.8	0.6	(*1*)
n-$C_6F_{13}NCO$	21.92	21.80	101.1	99.9	1.2	(*1*)
n-$C_7F_{15}NCO$	24.17	23.90	122.4	119.9	2.5	(*1*)
n-$C_8F_{17}NCO$	26.42	26.25	142.5	141.0	1.5	(*1*)
n-$C_9F_{19}NCO$	28.67	28.62	161.4	161.0	0.4	(*1*)
n-$C_{10}F_{21}NCO$	30.92	31.15	179.3	181.1	−1.8	(*1*)
n-$C_{11}F_{23}NCO$	33.17	33.80	196.5	201.1	−4.6	(*1*)
CF_3NO	7.96	7.93	−83.5	−84	0.5	(*13*)
C_2F_5NO	10.21	10.32	−43.7	−42	−1.7	(*13*)
n-C_3F_7NO	12.46	12.44	−9.5	−9.7	0.2	(*4*)
$CF_3CF(NO)CF_3$	12.46	12.21	−9.5	−13	3.5	(*20*)
n-C_4F_9NO	14.71	14.45	20.9	17.6	4.3	(*13*)
$C_2F_5CF(NO)CF_3$	14.71	14.95	20.9	24	−3.1	(*13*)
$(CF_3)_3CNO$	14.71	14.95	20.9	24	−3.1	(*20*)
n-$C_5F_{11}NO$	16.96	17.11	48.3	50	−1.7	(*13*)
n-$C_7F_{15}NO$	21.46	21.30	96.6	95	1.6	(*13*)
$OCF_2CF_2CF_2$	10.50	10.57	−39.0	−38	−1.0	(*16*)
$OCF_2CF(CF_3)CF(CF_3)$	15.00	15.03	24.6	25	−0.4	(*12*)
$OCF_2CF(CF_3)C(CF_3)_2$	17.25	17.24	51.6	51.5	−0.1	(*12*)
cis-$OCF_2CF(CF_3)C$-*n*-C_3F_7	19.50	19.84	76.5	80	−3.5	(*12*)
trans-$OCF_2CF(CF_3)C$-*n*-C_3F_7	19.50	19.65	76.5	78	−1.5	(*12*)
$OCF_2CF(CF_3)C(C_2F_5)_2$	21.75	21.51	99.4	97	2.4	(*12*)
$OCF_2CF(CF_3)C(n\text{-}C_3F_7)_2$	26.25	25.68	141.0	136	5.0	(*12*)
$OCF_2CF(CF_3)CF(n\text{-}C_7F_{15})$	28.50	28.62	160.0	161	−1.0	(*12*)
CF_3H	7.74	8.03	−87.7	−82.2	−5.5	(22)
CF_3CF_2H	9.99	10.04	−47.3	−46.5	−0.8	(22)
n-C_3F_7H	12.24	11.90	−12.6	−17.6	5.0	(22)
n-C_4F_9H	14.49	14.21	18.1	14.5	3.6	(22)
n-$C_5F_{11}H$	16.74	16.68	45.7	45	0.7	(22)
n-$C_6F_{13}H$	18.99	18.94	71.0	70.5	0.5	(22)
n-$C_7F_{15}H$	21.24	21.43	94.4	96.3	−1.9	(22)
n-$C_8F_{17}H$	23.49	23.69	116.1	118	−1.9	(*13*)
n-$C_9F_{19}H$	25.74	25.97	136.5	138.5	−2.0	(22)
n-$C_{10}F_{21}H$	27.99	28.44	155.8	159.5	−3.7	(22)
n-$C_{13}F_{27}H$	34.74	34.06	207.9	203	4.9	(22)
CF_3CFHCF_3	11.74	11.87	−19.9	−18	−1.9	(2)
$(CF_3)_3CH$	13.99	13.99	11.5	11.5	0.0	(2)

(Continued on page 381)

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

Compound	B.P.N.		B.P., °C.			
	Calcd.	Found	Calcd.	Found	Error	Ref.
 $CFH(CF_2)_4CF_2$	18.28	18.24	63.3	62.8	0.5	(*22*)
 $CFH(CF_2)_4CFCF_3$	20.53	20.46	87.2	86.5	0.7	(*22*)
 $CF_3CFCF_2CF(CF_3)CF_2CF(CF_3)CFH$	25.03	25.01	130.2	130	0.2	(*22*)
$CF_3OCF_2CF_2COF$	13.61	14.18	6.5	14	−7.5	(*5*)
$C_2F_5OCF_2CF_2COF$	15.86	15.84	35.2	35	0.2	(*5*)
n-$C_3F_7OCF_2CF_2COF$	18.11	17.90	61.4	59	2.4	(*5*)
n-$C_4F_9OCF_2CF_2COF$	20.36	20.03	85.4	82	3.4	(*5*)
n-$C_5F_{11}OCF_2CF_2COF$	22.61	22.32	107.8	105	2.8	(*5*)
n-$C_6F_{13}OCF_2CF_2COF$	24.86	24.67	128.7	127	1.7	(*5*)
n-$C_7F_{15}OCF_2CF_2COF$	27.11	27.07	148.4	148	0.4	(*5*)
n-$C_8F_{17}OCF_2CF_2COF$	29.36	29.74	167.0	170	−3.0	(*5*)
CF_3COOH	19.22	19.12	73.5	72.4	1.1	(*22*)
C_2F_5COOH	21.47	21.45	96.7	96.5	0.2	(*22*)
n-C_3F_7COOH	23.72	23.97	118.3	120.6	−2.3	(*22*)
n-C_4F_9COOH	25.97	26.08	138.5	139.5	−1.0	(*22*)
n-$C_5F_{11}COOH$	28.22	28.26	157.7	158	−0.3	(*22*)
n-$C_6F_{13}COOH$	30.47	30.49	175.8	176	−0.2	(*22*)
n-$C_7F_{15}COOH$	32.72	32.40	193.1	190.7	2.4	(*22*)
$C_2F_5SO_2F$	14.02	13.65	12.0	7	5.0	(*25*)
n-$C_3F_7SO_2F$	16.27	15.92	40.2	36	4.2	(*10*)
n-$C_4F_9SO_2F$	18.52	18.35	65.9	64	1.9	(*10*)
n-$C_5F_{11}SO_2F$	20.77	20.81	89.6	90	−0.4	(*25*)
n-$C_6F_{13}SO_2F$	23.02	23.26	111.7	114	−2.3	(*25*)
n-$C_7F_{15}SO_2F$	25.27	25.57	132.4	135	−2.6	(*10*)
n-$C_8F_{17}SO_2F$	27.52	27.78	151.8	154	−2.2	(*25*)
n-$C_{10}F_{21}SO_2F$	32.02	32.31	187.8	190	−2.2	(*25*)
n-$C_{12}F_{25}SO_2F$	36.52	36.73	220.6	222	−1.4	(*25*)
n-$C_{14}F_{29}SO_2F$	41.02	40.91	250.7	250	0.7	(*25*)
CF_3SF_5	12.12	11.71	−14.4	−20.4	6.0	(*8*)
$C_2F_5SF_5$	14.37	14.16	16.5	13.8	2.7	(*8*)
n-$C_3F_7SF_5$	16.62	16.42	44.3	42	2.3	(*15*)
n-$C_4F_9SF_5$	18.87	18.94	69.7	70.5	−0.8	(*15*)
n-$C_6F_{13}SF_5$	23.37	23.71	115.0	118.2	−3.2	(*7*)
$SF_5CF_2SF_5$	17.91	17.96	59.1	59.7	−0.6	(*8*)
$CF_3SF_4CF_2SF_5$	20.36	20.61	85.4	88.0	−2.6	(*8*)
$CF_3SF_4CF_2CF_2SF_5$	22.61	23.08	107.8	112.3	−4.5	(*8*)
$(CF_3)_2SF_4$	14.57	14.68	19.1	20.5	−1.4	(*6*)
$CF_3SF_4C_2F_5$	16.82	16.86	46.7	47.1	−0.4	(*26*)
$(C_2F_5)_2SF_4$	19.07	18.92	71.9	70.2	1.7	(*8*)
(*n*-$C_3F_7)_2SF_4$	23.57	23.48	116.9	116	0.9	(*15*)
(*n*-$C_4F_9)_2SF_4$	28.07	27.78	156.4	154	2.4	(*15*)
$CF_3SF_4SF_4CF_3$	20.56	20.56	87.5	87.5	0.0	(*26*)

at 760 mm., equals $T + \Delta T$. Equation 4 results (*23*) after starting with the Clapeyron equation $dP/dT = (\Delta HP)/(RT_b^2)$ and rewriting as

$$\Delta T = \frac{RT_b^2}{\Delta HP}\,\Delta P,$$

which letting C' equal $\Delta H/T_b$ (Trouton's Rule) then gives

$$\Delta T = \frac{RT_b}{C'P}\,\Delta P = CT_b\Delta P$$

In Table I, there are 10 new b.p.n.s for the atoms or groups substituted in perfluoroalkanes.

In Table II, there are observed and calculated boiling points and boiling point numbers of 83 substituted perfluoroalkanes. All calculations are manual, with emphasis on Equation 2 (new).

LIMITATION

As usual (*3*), some minor selection of data is necessary in each series. Exclusion of cyclic or branched compounds is necessary in perfluoromonocarboxylic acids, for statistical reasons. No substituted perfluoroalkenes such as $CF_2 = CFNO$ (*11*) are in Table II. Use of a uniform value of −1.83 for the atomic b.p.n. of carbon and 2.04 for fluorine, as in Equation 2, requires exclusion of 12 other series and approximately 90 other compounds.

DISCUSSION OF RESULTS

In Table II, the calculated normal boiling points of 83 substituted perfluoroalkanes have a root mean square error of only 2.6° (this is the first comparison on this basis) and a simple average error (*3*, *17*) of only 2.0°. The maximum error is 7.5° and only three errors exceed 5.0°.

A shielding effect is probably responsible for the lower b.p.n. of 2.95 for a lone secondary or tertiary hydrogen as compared with the b.p.n. of 3.45 for a lone primary hydrogen; see Table I for an explanation of the term lone hydrogen.

According to the b.p.n. of 14.93 for COOH in a perfluorocarboxylic acid, against 19.3 for COOH in RCH_2COOH (*17*), there should be less association in the perfluorocarboxylic acid.

The b.p.n. of 6.38 for NCO in perfluoroalkylisocyanates is reasonably close to the b.p.n. of 6.70 for NCO in $Ge(NCO)_4$ (*3*).

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Coupling of Fluoroalkyl Iodides

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The coupling of haloalkyl iodides by irradiation with ultraviolet light in the presence of mercury has been extended to fluorocarbons containing the carbon, hydrogen, chlorine, and iodine and the carbon, hydrogen, fluorine, and iodine groupings as the reactive sites. Both meso and racemic isomers of 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane and of 1,4-dichloro-1,1,2,3,4,4-hexafluorobutane have been prepared in high purity and characterized by measurement of physical properties and infrared and NMR spectra.

COUPLING of fluoroalkyl iodides to fluorocarbons containing twice as many carbon atoms as the original iodide by irradiation with ultraviolet light in the presence of mercury has been extended to compounds in which the reactive center is CHClI or CHFI.

2-Chloro-2-iodo-1,1,1-trifluoroethane, representing the CHClI structure, coupled under the combined influence of mercury and ultraviolet light to afford an 81% yield of a mixture of isomers of 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane, which could be separated by vapor-liquid phase chromatography (v.l.p.c.) into meso and racemic isomers. Identification of the isomers was made by independent synthesis.

Treatment of the dichlorohexafluorobutanes with bases under mild conditions resulted in removal of only one equivalent of hydrogen chloride. On the basis of a trans elimination, the 2-chloro-1,1,1,4,4,4-hexafluorobutene-2 derived from the meso butane was assigned the cis configuration; that from the racemic butane the trans configuration.

2,3-Dichloro-1,1,1,4,4,4-hexafluorobutane had been synthesized previously by Haszeldine (*3*) by addition of chlorine to *trans*-1,1,1,4,4,4-hexafluorobutene-2 in the presence of ultraviolet light; the product was incompletely characterized, and no discussion of isomer distribution was presented. On the basis of the reported boiling point of 78°, it would appear that Haszeldine's material was primarily the racemic isomer (b.p. 76.9°). However, when the author repeated this work, a mixture of racemic and meso isomers in nearly equal amounts was obtained. This is not inconsistent with Haszeldine's reported boiling point because that measurement was made by the micro capillary method which tends to give the boiling point of the lowest boiling component of a mixture. The formation of both butane isomers from a single butene isomer indicates both stepwise addition of the two chlorine atoms and the existence of a planar intermediate at some point in the process. Both are expected in a free radical process.

1-Chloro-2-iodo-1,1,2-trifluoroethane was employed as a representative of the CHFI type of fluorocarbon iodide. It coupled less readily than 2-chloro-2-iodo-1,1,1-trifluoroethane but like it yielded both racemic and meso isomers, which were obtained in high purity by preparative scale v.l.p.c. The assignment of configuration was made on the basis of a comparison of physical properties of the two isomers with those of the two closely related 2,3-dichloro-1,1,1,4,4,4-hexafluorobutanes. In both cases, the racemic configuration was assigned to the isomer having the shorter v.l.p.c. retention time, the lower melting point, the lower boiling point, the lower heat of vaporization, and the lower Trouton ratio. The NMR spectra appeared to be in accord with this assignment.

EXPERIMENTAL

The vapor pressure equations and constants derived therefrom were obtained in the manner described earlier (*1*). Infrared absorption bands were measured in the vapor phase on a Perkin-Elmer Model 137 Infracord spectrometer and are