Boiling Points and Boiling Point Numbers of *n*-Chlorofluoroalkanes

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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 satisfactory results in calculations of normal boiling points of 153 *n*-chlorofluoroalkanes, each of which contains at least one hydrogen, at least one chlorine, at least one fluorine, and two to five carbon atoms in a straight chain; the simple average error is 4.9°. Calculations of total boiling point number (b.p.n.) involve use of 16 different new b.p.n.'s of groups—rather than use of individual atomic b.p.n.'s for carbon, hydrogen, fluorine, and chlorine. For instance, the total b.p.n. of $CF_3CH_2CH_2CH_2Cl$ equals the b.p.n. of the CF_3 group plus twice the b.p.n. of the CH_2 group plus the b.p.n. of the CH_2Cl group.

SATISFACTORY results occur from application of the Kinney equation (*19*):

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

in calculations of the normal boiling points of hydrocarbons (*19–21*), silanes and organosilicon compounds (*23*), germanes and alkylgermanium compounds (*2*), boranes and alkylboron compounds (*3*), alkyl derivatives of bivalent sulfur, selenium, and tellurium, organic derivatives of trivalent phosphorus, and arsenic (*4*), perfluoroalkanes, perfluorocycloalkanes, and perfluoroalkenes (*5*), and numerous substituted perfluoroalkanes (*5, 6*). In the immediately previous publication (*6*) the equation:

$$\text{total boiling point number} = a + b(\text{number of carbon atoms}) + c \qquad (2)$$

together with Equation 1 allows a very accurate fit (simple average error, 1.2°) in calculations of normal boiling points of 108 perfluoroalkyl chlorides, bromides, and iodides.

The present manuscript correlates the boiling points of 153 *n*-chlorofluoroalkanes; these contain at least one hydrogen, at least one chlorine, at least one fluorine, and two

Table I. Boiling Point Numbers of Groups

Group	B.P.N.	No.[a]
CH_3	4.925	51
CH_2Cl	9.993	41
CH_2F	6.666	8
$CHCl_2$	12.528	23
$CHClF$	8.932	18
CHF_2	5.296	23
CCl_3	15.308	15
CCl_2F	10.838	18
$CClF_2$	6.872	42
CF_3	3.141	33
CH_2	3.465	40
$CHCl$	6.871	29
CHF	3.919	5
CCl_2	9.479	16
$CClF$	5.501	16
CF_2	2.219	53

[a] No. is number of examples—counting each group only once in any single compound.

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.
			a = Ethane derivatives, C_2			
$CClF_2CHF_2$	12.17	12.35	−13.6	−11	−2.6	(*24*)
CF_3CHClF	12.07	12.56	−15.1	−8	−7.1	(*12*)
$CClF_2CHClF$	15.80	15.28	34.5	28.1	6.4	(*24*)
CCl_2FCHF_2	16.13	15.45	38.5	30.2	8.3	(*14*)
CF_3CHCl_2	15.67	15.33	32.9	28.7	4.2	(*32*)
$CClF_2CHCl_2$	19.40	19.07	75.4	71.9	3.5	(*24*)
$CCl_2FCHClF$	19.77	19.13	79.3	72.5	6.8	(*24*)
CHF_2CCl_3	20.60	19.17	87.9	73.0	14.9	(*24*)
CCl_2FCHCl_2	23.37	23.54	115.0	116.6	−1.6	(*24*)
$CHClFCCl_3$	24.24	23.56	123.1	116.8	6.3	(*24*)
CF_3CH_2Cl	13.13	13.61	−0.1	6.5	−6.6	(*24*)
CHF_2CHClF	14.23	14.41	14.7	17	−2.3	(*32*)
$CClF_2CH_2F$	13.54	14.02	5.5	12	−6.5	(*13*)
$CClF_2CH_2Cl$	16.87	16.81	47.3	46.5	0.8	(*24*)
CHF_2CHCl_2	17.82	17.94	58.1	59.5	−1.4	(*24*)
CCl_2FCH_2F	17.50	16.97	54.5	48.4	6.1	(*8*)
$CHClFCHClF$	17.86	17.95	58.6	59.6	−1.0	(*8*)
CCl_2FCH_2Cl	20.83	20.65	90.2	88.4	1.8	(*24*)
$CHClFCHCl_2$	21.46	22.01	96.6	102	−5.4	(*24*)
$CClF_2CH_3$	11.80	12.46	−19.0	−9.5	−9.5	(*24*)
CHF_2CH_2Cl	15.29	15.85	28.2	35.1	−6.9	(*24*)
CCl_2FCH_3	15.76	15.59	34.0	31.9	2.1	(*24*)
$CHClFCH_2Cl$	18.93	19.25	70.4	73.8	−3.4	(*24*)
$CHClFCH_3$	13.86	14.34	9.8	16.2	−6.4	(*24*)
CH_2FCH_2Cl	16.66	17.35	44.8	52.8	−8.0	(*24*)

(*Continued on page 215*)

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

	B.P.N.		B.P., °C.			
Compound	Calcd.	Found	Calcd.	Found	Error	Ref.
b = Linear propane derivatives, C_3						
CF_3CF_2CHClF	14.29	14.64	15.5	20	−4.5	(*24*)
$CF_3CHClCF_3$	13.15	14.24	0.2	14.8	−14.6	(*24*)
$CHF_2CF_2CClF_2$	14.39	14.72	16.8	21	−4.2	(*24*)
$CF_3CHFCClF_2$	13.93	14.33	10.7	16	−5.3	(*22*)
$CF_3CF_2CHCl_2$	17.89	16.72	58.9	45.5	13.4	(*24*)
$CF_3CClFCHClF$	17.57	17.63	55.3	56	−0.7	(*24*)
$CF_3CHClCClF_2$	16.88	17.14	47.4	50.4	−3.0	(*24*)
$CClF_2CF_2CHClF$	18.02	17.28	60.4	52	8.4	(*24*)
$CClF_2CClFCHF_2$	17.67	17.63	56.4	56	0.4	(*24*)
$CF_3CHClCCl_2F$	20.85	20.52	90.4	87.1	3.3	(*24*)
$CClF_2CF_2CHCl_2$	21.62	20.96	98.1	91.5	6.6	(*24*)
$CClF_2CCl_2CHF_2$	21.65	21.03	98.4	92.3	6.1	(*24*)
$CClF_2CClFCHClF$	21.30	20.79	95.0	89.8	5.2	(*24*)
CCl_2FCF_2CHClF	21.99	20.86	101.8	90.5	11.3	(*24*)
$CClF_2CHClCClF_2$	20.62	20.61	88.1	88	0.1	(*17*)
$CF_3CCl_2CHCl_2$	25.15	24.54	131.3	125.8	5.5	(*24*)
$CHF_2CCl_2CCl_2F$	25.61	25.52	135.4	134.6	0.8	(*24*)
$CClF_2CHClCCl_2F$	24.58	24.86	126.2	128.7	−2.5	(*24*)
$CClF_2CClFCHCl_2$	24.90	24.98	129.0	129.8	−0.8	(*24*)
$CCl_2FCF_2CHCl_2$	25.58	24.67	135.1	127	8.1	(*24*)
$CClF_2CCl_2CHCl_2$	28.88	29.54	163.1	168.4	−5.3	(*24*)
$CHF_2CCl_2CCl_3$	30.08	30.31	172.8	174.6	−1.8	(*24*)
$CCl_2FCHClCCl_2F$	28.55	29.41	160.4	167.4	−7.0	(*24*)
$CHCl_2CF_2CCl_3$	30.06	30.07	172.6	172.7	−0.1	(*24*)
$CCl_3CHClCClF_2$	29.05	29.64	164.5	169.2	−4.7	(*29*)
$CHCl_2CCl_2CCl_2F$	32.85	35.02	194.1	210	−15.9	(*24*)
$CCl_2FCHClCCl_3$	33.02	34.61	195.3	207	−11.7	(*24*)
$CHClFCCl_2CCl_3$	33.72	35.02	200.5	210	−9.5	(*24*)
$CF_3CF_2CH_2Cl$	15.35	15.21	29.0	27.2	1.8	(*24*)
$CF_3CH_2CClF_2$	13.48	15.30	4.7	28.4	−23.7	(*24*)
$CClF_2CF_2CH_2F$	15.76	15.93	34.0	36.1	−2.1	(*10*)
CHF_2CF_2CHClF	16.45	16.58	42.4	43.9	−1.5	(*10*)
$CClF_2CF_2CH_2Cl$	19.08	18.71	72.0	68.0	4.0	(*16, 28*)
$CHF_2CClFCHClF$	19.73	19.46	78.9	76	2.9	(*24*)
$CF_3CH_2CCl_3$	21.91	21.31	101.0	95.1	5.9	(*18*)
$CF_3CHClCHCl_2$	22.54	22.42	107.1	106	1.1	(*24*)
$CF_3CCl_2CH_2Cl$	22.61	22.27	107.8	104.5	3.3	(*24*)
$CCl_2FCF_2CH_2Cl$	23.05	22.73	112.0	108.9	3.1	(*24*)
$CHF_2CCl_2CHCl_2$	27.30	27.02	150.0	147.6	2.4	(*24*)
$CClF_2CH_2CCl_3$	25.65	25.23	135.3	132	3.3	(*24*)
$CCl_3CF_2CH_2Cl$	27.52	27.42	151.8	151.0	0.8	(*24*)
$CClF_2CF_2CH_3$	14.02	14.63	11.9	19.9	−8.0	(*24*)
$CHF_2CF_2CH_2Cl$	17.51	17.45	54.6	54	0.6	(*9*)
$CF_3CCl_2CH_3$	17.54	17.00	55.0	48.8	6.2	(*24*)
$CF_3CHClCH_2Cl$	20.01	19.52	81.8	76.7	5.1	(*24*)
$CF_3CH_2CHCl_2$	19.13	19.14	72.5	72.6	−0.1	(*24*)
$CH_3CF_2CCl_2F$	17.98	18.00	59.9	60.2	−0.3	(*24*)
$CH_3CClFCClF_2$	17.30	17.60	52.2	55.6	−3.4	(*24*)
$CH_3CF_2CCl_3$	22.45	21.98	106.3	101.7	4.6	(*24*)
$CClF_2CHClCH_2Cl$	23.74	23.22	118.4	113.6	4.8	(*24*)
$CClF_2CH_2CHCl_2$	22.87	22.61	110.3	107.8	2.5	(*24*)
$CCl_2FCClFCH_3$	21.26	21.58	94.6	97.7	−3.1	(*24*)
$CClF_2CCl_2CH_3$	21.28	20.83	94.8	90.2	4.6	(*24*)
$CHCl_2CF_2CH_2Cl$	24.74	24.71	127.6	127.3	0.3	(*16*)
$CH_3CClFCCl_3$	25.73	26.09	136.4	139.6	−3.2	(*24*)
$CCl_2FCHClCH_2Cl$	27.70	27.84	153.3	154.5	−1.2	(*31*)
$CF_3CH_2CH_2Cl$	16.60	16.71	44.1	45.4	−1.3	(*24*)
$CF_3CHClCH_3$	14.94	15.43	23.8	30	−6.2	(*24*)
$CClF_2CHClCH_3$	18.67	18.88	67.5	69.8	−2.3	(*24*)
$CH_3CF_2CHCl_2$	19.67	19.74	78.3	79.0	−0.7	(*24*)
$CH_2ClCF_2CH_2Cl$	22.21	21.47	103.9	96.7	7.2	(*24*)
$CClF_2CH_2CH_2Cl$	20.33	19.91	85.1	80.8	4.3	(*26*)
$CH_3CHClCCl_2F$	22.63	23.21	108.0	113.5	−5.5	(*24*)
$CH_2ClCClFCH_2Cl$	25.49	25.10	134.3	130.8	3.5	(*24*)
$CH_3CClFCHCl_2$	22.95	23.55	111.0	116.7	−5.7	(*24*)
$CCl_2FCH_2CH_2Cl$	24.30	23.72	123.6	118.3	5.3	(*31*)
$CH_3CH_2CClF_2$	15.26	15.06	27.8	25.4	2.4	(*24*)
$CH_3CF_2CH_2Cl$	17.14	17.55	50.4	55.1	−4.7	(*24*)
$CH_3CHClCHF_2$	17.09	17.28	49.8	52	−2.2	(*24*)
$CH_3CHFCHClF$	17.78	17.36	57.7	52.9	4.8	(*24*)
$CH_3CH_2CCl_2F$	19.23	18.58	73.6	66.6	7.0	(*24*)
$CH_3CClFCH_2Cl$	20.42	20.66	86.1	88.5	−2.4	(*24*)

(*Continued on page 216*)

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.
b = Linear propane derivatives, C_3 (*cont.*)						
$CH_3CHClCHClF$	20.73	21.10	89.2	93	−3.8	(*24*)
$CH_2ClCHClCH_2F$	23.53	23.75	116.5	118.5	−2.0	(*24*)
$CH_2ClCHFCH_2Cl$	23.91	24.56	120.0	126	−6.0	(*7*)
$CH_2FCH_2CH_2Cl$	20.12	20.04	83.0	82.1	0.9	(*24*)
$CH_3CClFCH_3$	15.35	15.86	29.0	35.2	−6.2	(*1, 17*)
CH_3CHFCH_2Cl	18.84	18.71	69.4	68	1.4	(*1*)
c = Linear butane derivatives, C_4						
$CClF_2CF_2CF_2CHF_2$	16.61	17.11	44.2	50	−5.8	(*24*)
$CF_3CF_2CF_2CHCl_2$	20.11	19.50	82.9	76.5	6.4	(*24*)
$CF_3CHClCCl_2CF_3$	22.63	22.32	108.0	105	3.0	(*24*)
$CF_3CF_2CF_2CH_2Cl$	17.57	17.45	55.3	54	1.3	(*24*)
$CF_3CF_2CClFCH_2Cl$	20.85	19.08	90.4	72.0	18.4	(*24*)
$CF_3CHClCHClCF_3$	20.02	19.65	81.9	78	3.9	(*24*)
$CF_3CH_2CF_2CCl_3$	24.13	24.07	122.1	121.5	0.6	(*24*)
$CClF_2CHClCHClCClF_2$	27.49	25.91	151.6	138	13.6	(*25*)
$CF_3CHClCH_2CF_3$	16.62	17.19	44.3	51	−6.7	(*24*)
$CH_3CF_2CF_2CCl_3$	24.67	24.24	127.0	123.1	3.9	(*24*)
$CH_3CF_2CCl_2CHCl_2$	29.15	29.34	165.3	166.8	−1.5	(*24*)
$CClF_2CH_2CF_2CH_3$	17.48	18.86	54.3	69.6	−15.3	(*24*)
$CF_3CH_2CCl_2CH_3$	21.01	20.80	92.1	89.9	−2.2	(*24*)
$CF_3CH_2CH_2CHCl_2$	22.60	22.84	107.7	110	−2.3	(*24*)
$CF_3CH_2CHClCH_2Cl$	23.47	23.37	115.9	115	0.9	(*24*)
$CClF_2CH_2CHFCH_2Cl$	24.25	23.75	123.2	118.5	4.7	(*24*)
$CCl_2FCH_2CF_2CH_3$	21.45	22.08	96.5	102.7	−6.2	(*24*)
$CH_3CF_2CCl_2CH_2Cl$	26.62	26.28	144.2	141.2	3.0	(*24*)
$CH_3CF_2CH_2CCl_3$	25.92	26.03	138.1	139.1	−1.0	(*24*)
$CF_3CH_2CH_2CH_2Cl$	20.06	20.47	82.3	86.6	−4.3	(*24*)
$CF_3CH_2CHClCH_3$	18.40	18.49	64.6	65.6	−1.0	(*24*)
$CF_3CHClCH_2CH_3$	18.40	17.83	64.6	58.3	6.3	(*24*)
$CH_3CF_2CClFCH_3$	17.57	17.42	55.3	53.6	1.7	(*24*)
$CH_3CF_2CH_2CHClF$	19.54	19.89	76.9	80.6	−3.7	(*27*)
$CH_3CF_2CHClCH_2Cl$	24.01	24.24	120.9	123.1	−2.2	(*24*)
$CH_3CF_2CH_2CHCl_2$	23.14	23.83	112.8	119.3	−6.5	(*24*)
$CH_3CF_2CCl_2CH_3$	21.55	20.79	97.4	89.8	7.6	(*24*)
$CH_3CHClCF_2CH_2Cl$	24.01	23.45	120.9	115.7	5.2	(*24*)
$CH_2ClCF_2CH_2CH_2Cl$	25.67	26.40	135.9	142.3	−6.4	(*24*)
$CClF_2CHClCH_2CH_3$	22.13	21.50	103.1	97.0	6.1	(*24*)
$CHCl_2CF_2CH_2CH_3$	23.14	22.97	112.8	111.2	1.6	(*24*)
$CH_3CF_2CH_2CH_2Cl$	20.60	21.12	87.9	93.2	−5.3	(*24*)
$CH_3CF_2CHClCH_3$	18.94	19.12	70.5	72.4	−1.9	(*24*)
$CClF_2CH_2CH_2CH_3$	18.73	17.61	68.2	55.8	12.4	(*24*)
$CH_2ClCF_2CH_2CH_3$	20.60	20.10	87.9	82.7	5.2	(*24*)
$CCl_2FCH_2CH_2CH_3$	22.69	21.33	108.5	95.3	13.2	(*24*)
$CH_3CClFCHClCH_3$	22.22	22.64	104.0	108.1	−4.1	(*24*)
$CH_3CClFCH_2CH_2Cl$	23.88	24.31	119.8	123.7	−3.9	(*24*)
$CH_2FCH_2CH_2CH_2Cl$	23.59	23.34	117.1	114.7	2.4	(*24*)
$CH_3CClFCH_2CH_3$	18.82	18.68	69.2	67.7	1.5	(*24*)
d = Linear pentane derivatives, C_5						
$CClF_2CF_2CF_2CF_2CHF_2$	18.83	19.55	69.3	77	−7.7	(*24*)
$CClF_2CH_2CF_2CF_2CF_3$	17.92	18.90	59.2	70	−10.8	(*15*)
$CHF_2CF_2CF_2CF_2CH_2Cl$	21.95	22.32	101.4	105	−3.6	(*9*)
$CH_3CH_2CF_2CHClCH_2Cl$	27.47	26.91	151.4	146.7	4.7	(*24*)
$CH_2ClCH_2CF_2CH_2CH_2Cl$	29.13	30.53	165.2	176.3	−11.1	(*24*)
$CH_2ClCH_2CF_2CHClCH_3$	27.47	27.87	151.4	154.8	−3.4	(*24*)
$CClF_2CH_2CH_2CH_2CH_2Cl$	27.26	28.14	149.6	157	−7.4	(*11*)
$CH_3CH_2CF_2CH_2CH_2Cl$	24.07	23.68	121.5	117.9	3.6	(*24*)
$CH_3CH_2CF_2CHClCH_3$	22.41	21.75	105.9	99.4	6.5	(*24*)
$CH_2FCH_2CH_2CH_2CH_2Cl$	27.05	26.39	147.9	143.2	4.7	(*24*)

to five carbon atoms in a straight, saturated chain. In Table II the simple average difference in the normal boiling points of isomers is 12.5° in 207 combinations; the maximum difference is 59.4°; calculations must allow adequately for these differences. Satisfactory allowance for isomers occurs through calculations of the total boiling point number using the 16 different new b.p.n.'s of groups in Table I. For a random example, obtain the total b.p.n. of $CF_3CH_2CH_2CH_2Cl$ by adding the b.p.n. of the CF_3 group, the b.p.n. of the CH_2Cl, and twice the b.p.n. of the CH_2 group. A digital computer operated by Edward Klucznik furnishes a mathematical evaluation of the 16 new b.p.n.'s of groups through a least squares fit to a standard linear regression model. Calculations of the normal boiling points of 153 compounds in Table II involve first finding the total b.p.n. of the individual compound according to the new equation:

$$\text{total boiling point number} = aA + bB + cC + dD + eE \qquad (3)$$

and then calculating the normal boiling point according to Equation 1. Usually the coefficients *a*, *b*, *c*, *d*, and *e* are one, although values of 2 and 3 sometimes occur; one to five different groups are present.

LIMITATION

Insufficiency of examples causes exclusion of compounds with only one or more than five carbon atoms, or with branched or cyclic structure. Occurrence of the CHF group only five times and the CH_2F group only eight times (Tables I and II) limits the accuracy of fit of the new b.p.n.'s. Assumption that each group in the molecule is independent of any other group present involves some approximation. Group b.p.n.'s herein do not properly fit compounds with a lone hydrogen atom such as $CF_3CF_2CHF_2$ (*5*). Myer's equation (*30*) introduces rather minor errors in normal boiling points corrected from the usual pressures above 700 mm. pressure.

DISCUSSION OF RESULTS

New Equation 3 is for calculations of total boiling point number of *n*-chlorofluoroalkanes through use of the new boiling point numbers of 16 groups, such as CH_2Cl. Then the Kinney equation, Equation 1, serves in calculation of 153 normal boiling points of *n*-chlorofluoroalkanes, with a simple average error of 4.9°, a root mean square error of 6.2°, a standard deviation of 0.65 in the total boiling point number, and 90.8% of the calculated boiling points within 10° of the observed b.p.'s. Kinney (*20*) has 87.4% of 437 calculated boiling points within 10° of the observed b.p.'s of aliphatic, alicyclic, and aromatic monohalogen derivatives.

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Received for review January 6, 1966. Accepted February 10, 1967.

Thermodynamic Excess Properties of Three Alcohol-Hydrocarbon Systems

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The thermodynamic functions ΔC_p, ΔH, ΔS^E, and ΔG^E are presented as functions of temperature over the entire composition range for three binary liquid systems. The pressure dependency of ΔH, ΔS^E, and ΔG^E is determined from measurements of ΔV.

THE PURPOSE of this paper is to present an extensive correlation of thermodynamic data for the binary liquid systems: ethanol-toluene, 1-propanol-*n*-heptane, and 2-propanol-*n*-heptane. The results presented provide data over a considerable temperature range on the excess heat capacities, enthalpies, entropies, Gibbs free energies, and volumes of three highly nonideal alcohol-hydrocarbon solutions.

The complexity of systems such as these on a molecular scale is demonstrated in another paper (*24*), where heat-of-mixing data are used in conjunction with infrared spectral data. The present paper is devoted to simple publication of results so that they may be of aid to anyone who wishes to test or to develop a theory.

The usual correlation of excess properties of mixing for binary systems represents a property, say ΔM^E, as a function of mole fraction for a particular temperature by an equation such as

$$\frac{\Delta M^E}{x_1 x_2} = \sum_{n=0}^{n} A_n (x_1 - x_2)^n$$

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