[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

PHYSICAL PROPERTIES OF *n*-PERFLUOROALKYL HALIDES AND DIHALIDES AND A COMPARISON WITH THE CORRESPONDING ALKYL COMPOUNDS[1]

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The dynamic field of fluorocarbon chemistry, now in a state of continuous growth, is emerging as a segment of chemistry which is destined to become as immense as that branch of the chemistry of carbon compounds known as organic. The striking differences in the chemical and physical properties of the fluorocarbons and hydrocarbons have been reported previously (1–4). As part of a general program of studies on the preparation and properties of fluorocarbon derivatives, we are now reporting a comparison of some physical properties of a series of *n*-perfluoroalkyl halides and dihalides with the corresponding hydrocarbon derivatives. This study is made possible by the recently developed general method of synthesizing perfluoroalkyl halides and dihalides of known structures and in high purity by the action of halogen on the corresponding silver perfluoro-carboxylic acid salt (5–13).

It is convenient to compare first the physical constants of the fluorocarbon and hydrocarbon *n*-alkyl halide series.

NORMAL BOILING POINTS

In comparing the boiling points of perfluoroalkyl halides at atmospheric pressure with the analogous hydrocarbons (Table I), the strikingly lower boiling points of the fluorocarbon derivatives, in spite of their much higher molecular weights, are immediately evident. The same low intermolecular attractive forces apparent in fluorocarbons are operative in the monohalogenated fluorocarbon derivatives. The increment per CF_2 group in a homologous series is of the same order of magnitude as the CH_2 increment for the hydrocarbon derivatives with both decreasing gradually in moving up a homologous series. Also, as is known to be the case for *n*-alkyl halides, the boiling points of the halides of any particular perfluoroalkyl group always increase in the order Cl → Br → I. The boiling point differences are always greater between iodides and bromides than between bromides and chlorides.

DENSITIES AND MOLAR VOLUMES

The densities of those compounds which were liquids at room temperature were determined in the standard manner employing pycnometers of *ca.* 3 cc. and 1.5 cc. capacities. The dilatometer method was used for those compounds which were gases at room temperature. The dilatomer, of about 3 cc. capacity, was sealed on to a high vacuum system, the halide was distilled into it, and then

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it was sealed off. The volume was measured at several temperatures and the corresponding densities calculated after the weight of the contents had been determined. The weighings were corrected to vacuum and for the vapor present.

Table II gives the experimentally determined densities, while Table III and Figure 2 correlate the data by comparing the densities of fluorocarbon and hydrocarbon alkyl halides at "corresponding" temperatures, *i.e.*, normal boiling points. The densities of the *n*-alkyl halides were corrected to the N.B.P. by using a second-order equation (14). The densities of the perfluoroalkyl halides were extrapolated to the boiling points by means of a graphical method. A plot of density *vs.* fraction of the absolute boiling point was made using the values for *n*-C_5F_{12} (15) and $C_8F_{15}Cl$ (16). These curves were demonstrated to be essentially identical, although displaced. By applying the former curve to the points of a similar graph for the perfluoroalkyl halides, the latter density values at N.B.P. could be read from the graph to three decimal places.

TABLE I

BOILING POINTS (760 MM.) OF FLUOROCARBON AND HYDROCARBON *n*-ALKYL HALIDES[a]

HALOGEN	CH_3	CF_3	C_2H_5	C_2F_5	C_3H_7	C_3F_7	C_5H_{11}	C_5F_{11}
Cl..........	−23.73	−82[b]	13.1	−38	46.60	−2	108.4	59.5
Br..........	4.5	−59	38.40	−21	71.00	12	127.9	73.9
I..........	42.50	−22.5[c]	72.30	12.5	102.45	41.2	154.2	94.4

[a] The values for the hydrocarbon derivatives in this table and those following were taken from Beilstein's "Handbuch der organischen Chemie," the "International Critical Tables," the Landolt-Boernstein "Physikalisch-chemische Tabellen," and J. Timmerman's book "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., 1950.

Unless otherwise noted, the physical constants of the fluorocarbon derivatives were taken from references 5–9.

[b] Ruff and Keim, *Z. anorg. u. allgem. Chem.*, **201**, 255 (1931).

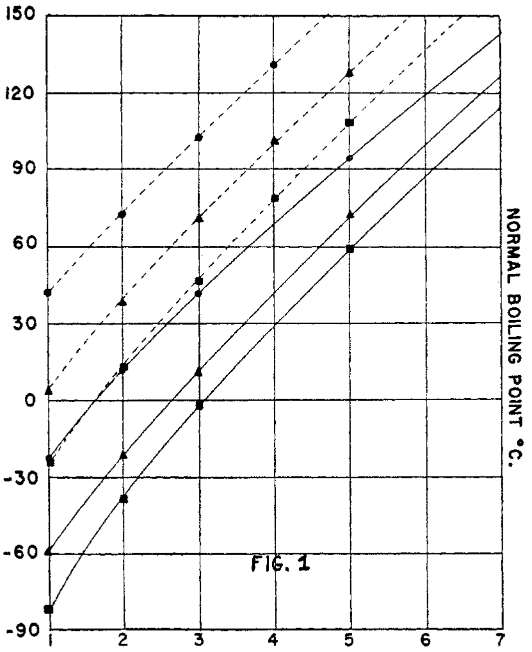
[c] Banks, Emeléus, Haszeldine, and Kerrigan, *J. Chem. Soc.*, 2188 (1948).

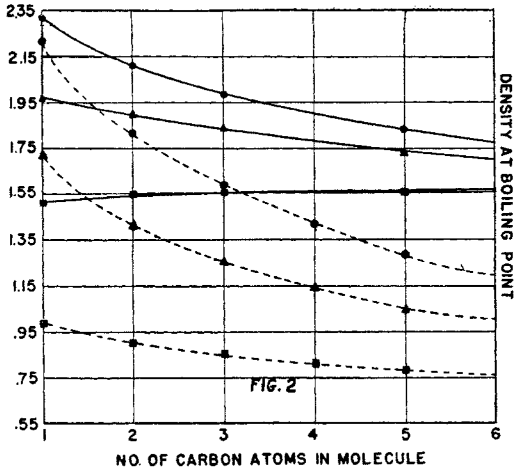
As would be expected, for any given alkyl group the density increases in the order Cl → Br → I, with the fluorocarbon derivatives always possessing the greater density. However, the relative increase in density by replacing a chlorine with a bromine or iodine is greater for the hydrocarbon derivatives. An increment of CF_2 or CH_2 lowers the density in all cases with the exception of the perfluoroalkyl chlorides.

The molecular volumes compared at corresponding temperatures (Figure 3 and Table III) form a straight-line relationship within experimental accuracy. The average increment per CF_2 group is 32 cc./mole as compared with 21 cc./mole per CH_2 group.

REFRACTIVE INDEX AND MOLECULAR REFRACTION

An Abbe refractometer was used for the determination of indices of refraction of those compounds of $n_D > 1.3000$, while a special refractometer (1) was em-





HYDROCARBON AND FLUOROCARBON *n*-ALKYL HALIDES

FIG. 1. NORMAL BOILING POINTS

FIG. 2. DENSITIES AT THE NORMAL BOILING POINT

Hydrocarbon iodides, ●---------●; hydrocarbon bromides, ▲---------▲; hydrocarbon chlorides, ■---------■; fluorocarbon iodides, ●————●; fluorocarbon bromides, ▲————▲; fluorocarbon chlorides, ■---------■

ployed when $n_D > 1.3000$. Both refractometers were adapted for determinations at low temperatures by a previously described method (17).

Pure fluorocarbons are known to have refractive indices which are lower than any other known type of organic compounds. It is not surprising to find that this striking property is carried over in large measure to the perfluoroalkyl halides. The refractive indices of the fluorocarbon derivatives are very much lower than the corresponding hydrocarbon derivatives (Table IV). The indices for one particular alkyl group always increase in the order Cl → Br → I. In figure 4 the molecular refractions are compared, using the Lorentz-Lorenz formula of the two series of halides. Since the atomic refraction of fluorine (1.23) is very close to that of hydrogen (1.10) the values for the two series are very close in contrast to molecular volumes (compare Figures 4 and 3). The

TABLE II

DENSITIES OF FLUOROCARBON *n*-ALKYL HALIDES

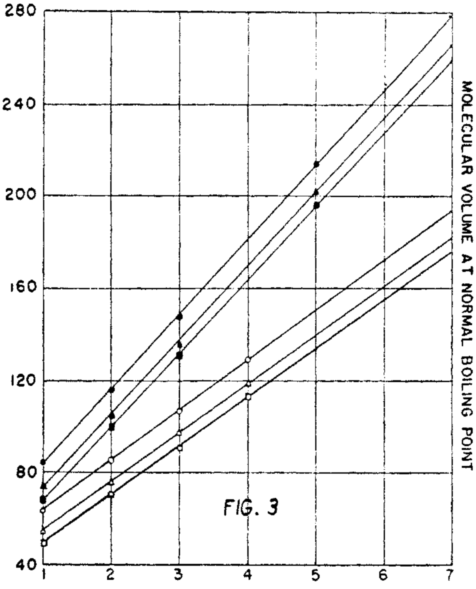
HALOGEN	CF_3X		C_2F_5X		C_3F_7X		$C_5F_{11}X$	
	d_4^t	t, °C.	d_4^t	t, °C.	d_4^t	t, °C.	d_4^t	t, °C.
Cl	1.726[a]	−130	1.6914	−78.5	1.6605	−33.5	1.7150	0.0
	1.296[b]	−30	1.5678	−42.2	1.5572	0.0	1.6450	25.8
Br	1.94[c]	−54	1.9492	−32.2	1.9845	−32.2	1.9324	0.0
	1.78[c]	−18	1.8098	0.0	1.8746	0.0	1.8522	28.4
I	2.5485[d]	−78.5	2.1605	0.0	2.1306	0.0	2.1141	0.0
	2.3608[d]	−32.5	2.0718	23.5	2.0337	28.5	2.0349	27.8

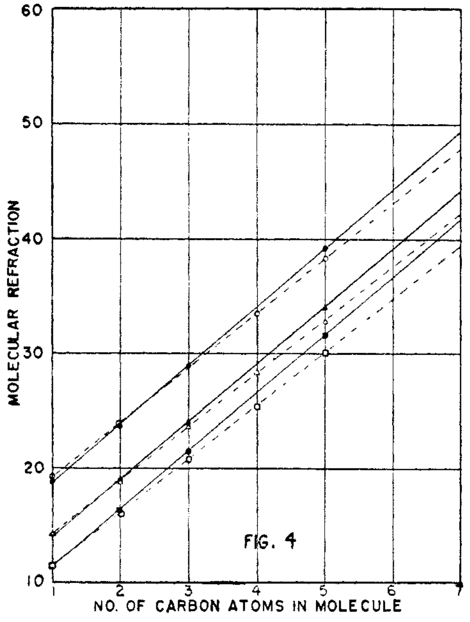
[a] Ruff, and Keim, *Z. anorg. u. allgem. Chem.*, **201**, 255 (1931). [b] Kinetic Chemicals, Technical Bulletin *Freon Compounds*. [c] Minnesota Mining and Manufacturing Co., Technical Bulletin, *Trifluorobromomethane*. [d] Nodiff, Grosse, and Hauptschein, unpublished data.

TABLE III

DENSITIES AND MOLECULAR VOLUMES AT THE NORMAL BOILING POINT OF FLUOROCARBON AND HYDROCARBON *n*-ALKYL HALIDES

COMPOUND	$d_4^{b.p.}$		M.V.$^{b.p}$	
	H	F	H	F
CX_3Cl	0.9915	1.533	50.92	68.15
CX_3Br	1.7206	1.96	55.18	76.1
CX_3I	2.2174	2.316	64.02	84.60
C_2X_5Cl	0.9062	1.555	71.20	99.34
C_2X_5Br	1.4223	1.902	76.62	104.6
C_2X_5I	1.8149	2.114	85.94	116.3
C_3X_7Cl	0.8581	1.564	91.54	130.7
C_3X_7Br	1.2620	1.833	97.47	135.8
C_3X_7I	1.5844	1.988	107.30	148.9
$C_5X_{11}Cl$	0.793	1.551	134	196.3
$C_5X_{11}Br$	1.077	1.722	140.3	202.7
$C_5X_{11}I$	1.316	1.839	150.5	215.3





HYDROCARBON AND FLUOROCARBON n-ALKYL HALIDES

FIG. 3. MOLECULAR VOLUMES AT THE NORMAL BOILING POINT

FIG. 4. MOLECULAR REFRACTIONS

Fluorocarbon iodides, ●———●; fluorocarbon bromides, ▲———▲; fluorocarbon chlorides, ■———■; hydrocarbon iodides, ○----------○; hydrocarbon bromides, △----------△; hydrocarbon chlorides, □----------□

average increment per CF_2 group is 5.1 cc./mole as compared with 4.5 cc./mole per CH_2 group. Both series show a straight-line relationship. With the possible exception of the one-carbon halides, the molar refractions are slightly higher for the perfluoroalkyl series. The slope of the latter is greater.

For the sake of brevity, the boiling points, molar refractions, and molar volumes of the perfluoropolymethylene dihalides as compared to the corresponding "hydrocarbon" polymethylene dihalides are summarized in Tables V, VI, and VII. Figures 5, 6, and 7 show these relations graphically, and require no further comments.

TABLE IV

INDICES OF REFRACTION AND MOLAR REFRACTIONS OF FLUOROCARBON AND HYDROCARBON *n*-ALKYL HALIDES

COMPOUND	H		F		H	F
	n_D^t	t	n_D^t	t	M.R.$_D^{LL}$	
CX_3Cl	1.3712	−23.7			11.62	
CX_3Br	1.4269	4.5			14.64	
CX_3I	1.5311	20	1.3710 1.3790	−29.8 −42.2	19.27	18.90
C_2X_5Cl	1.3724	13.1	1.2678	−42.2	16.29	16.60
C_2X_5Br	1.4130	38.4	1.2966 1.3040	−29.8 −42.2	19.10	18.97
C_2X_5I	1.5137	20	1.3378 1.3636	0.5 −42.2	24.25	23.74
C_3X_7Cl	1.3886	20	1.2781 1.2837	−29.8 −42.2	20.80	21.60
C_3X_7Br	1.4349	20	1.3070 1.3131	−29.8 −42.2	23.75	24.05
C_3X_7I	1.5057	20	1.3391 1.3624	0.5 −42.2	28.87	29.07
$C_5X_{11}Cl$	1.4119	20	1.2736 1.2845	25.4 0.0	28.84	31.77
$C_5X_{11}Br$	1.4444	20	1.2920 1.3042	27.8 0.0	32.98	34.19
$C_5X_{11}I$	1.4955	20	1.3243 1.3389	31.5 0.5	38.30	39.18

PROPERTIES OF UNKNOWN HALIDES

The above correlations permit one to predict with reasonable accuracy the physical properties of the as yet unknown *n*-perfluorobutyl and *n*-perfluorohexyl halides. Their properties are given in Table VIII.

TABLE V

Normal Boiling Points of Fluorocarbon and Hydrocarbon Polymethylene Dihalides

HALOGEN	$X(CF_2)_2X$	$X(CH_2)_2X$	$X(CF_2)_3X$	$X(CH_2)_3X$	$X(CF_2)_4X$	$X(CH_2)_4X$
Cl	3.8[a]	83.5	35.7	125		161–163
Br	46.4[a]	131.65	74.2	167.3		197–198
I	113[b]		131	224	150	

[a] Locke, Brode, and Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934).

[b] Raasche, U. S. Patent 2,424,667, July 29, 1947.

TABLE VI

Molar Refractions of Fluorocarbon and Hydrocarbon Polymethylene Dihalides

HALOGEN	$X(CF_2)_2X$	$X(CH_2)_2X$	$X(CF_2)_3X$	$X(CH_2)_3X$	$X(CF_2)_4X$	$X(CH_2)_4X$
Cl	21.34[a]	20.98	26.52	25.11		30.16
Br		26.95	31.90	31.18		
I	38.88[b]		42.19	41.83	46.98	46.43

[a] See reference [a], Table V for density and refractive index values which were used for this calculation.

[b] See reference [b], Table V, for density and refractive index values which were used for this calculation.

TABLE VII

Molar Volumes at 20°C. of Fluorocarbon and Hydrocarbon Polymethylene Dihalides

HALOGEN	$X(CF_2)_2X$	$X(CH_2)_2X$	$X(CF_2)_3X$	$X(CH_2)_3X$	$X(CF_2)_4X$	$X(CH_2)_4X$
Cl	116.3[a]	78.80	140.6	95.0		111
Br	120[a]	86.16	144.9	102		121
I	136[b]		156.4	115	182.1	135

[a] See reference [a], Table V. [b] See reference *b*, Table V.

TABLE VIII

Calculated Properties of n-C_4F_9X and n-$C_6F_{13}X$

	N.B.P., °C.	MOLAR VOLUME AT B.P.	MOLAR REFRACTION	d AT[a] N.B.P.	n_D[a] AT N.B.P.
n-$CF_3(CF_2)_3Cl$	29	164	26.62	1.55	1.258
n-$CF_3(CF_2)_3Br$	43	169	29.2	1.77	1.275
n-$CF_3(CF_2)_3I$	69	181	34.1	1.91	1.302
n-$CF_3(CF_2)_5Cl$	87	227	36.7	1.56	1.256
n-$CF_3(CF_2)_5Br$	101	232	39.2	1.72	1.269
n-$CF_3(CF_2)_5I$	120	246	44.2	1.81	1.287

[a] Values calculated from molar volumes and molar refractions given in the above table.

The unknown values for the dihalides (Tables V, VI, and VII) may be interpolated in a similar manner.

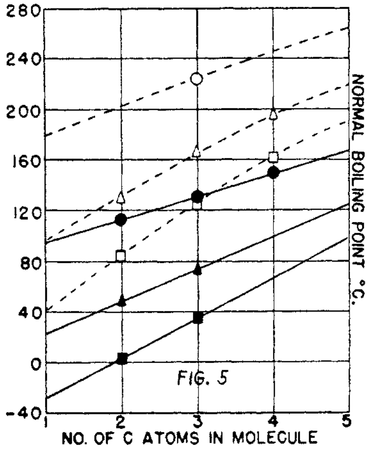


FIG. 5

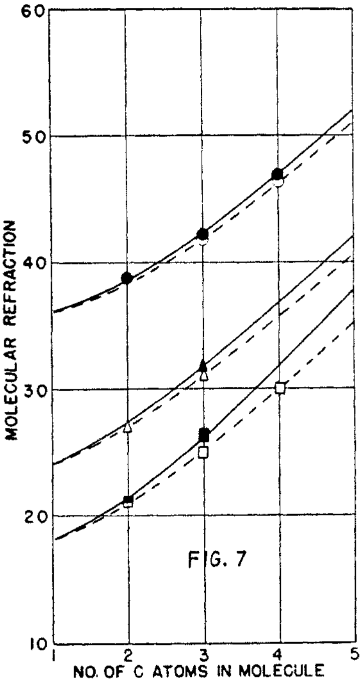


FIG. 7

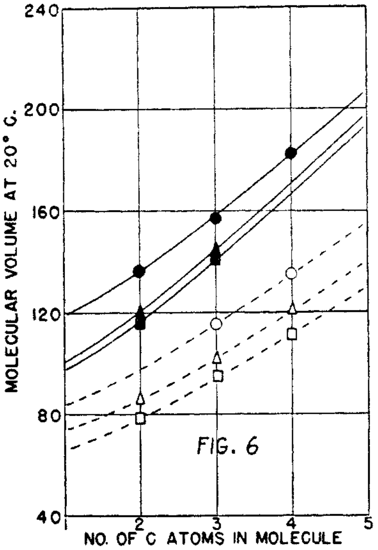


FIG. 6

FLUOROCARBON AND HYDROCARBON POLYMETHYLENE DIHALIDES

FIG. 5. NORMAL BOILING POINTS FIG. 7. MOLECULAR REFRACTIONS

FIG. 6. MOLECULAR VOLUMES AT 20°

Fluorocarbon diiodides, ●————●; fluorocarbon dibromides, ▲————▲; fluorocarbon dichlorides, ■————■; hydrocarbon diiodides, ○----------○; hydrocarbon dibromides, △----------△; hydrocarbon dichlorides, □----------□

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SUMMARY

Various physical constants of perfluoroalkyl halides and dihalides have been correlated and compared with the corresponding "hydrocarbon" analogs. Such a

correlation enables one to predict with reasonable accuracy certain properties of unknown chemical individuals fitting into the field covered by this survey.

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Note added to proof (January 29, 1953): R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952) has confirmed our findings for the perfluoro *n*-propyl and *n*-amyl halides and our predictions for the normal boiling points of the compounds of Table VIII (found N.B.P., °C. 30, 44, 67, 86, 100 and 117°, respectively).