Molar Refractivity in Fluorine-Containing Perhalo Compounds[1]

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A new set of atomic and group refractions is proposed for fluoroperhalo compounds, based on refractivity data for 112 compounds carefully screened for evidence of purity. Molar refractions found for saturated perhaloalkanes are fitted to ±0.1%, and for terminally unsaturated perhalo olefins to ±0.2%. The set employs single, invariant values for carbon and for fluorine, but multiple values, dependent on position, for the other halogens.

The experimentally determined Lorentz–Lorenz molar refractions, R_{exp},[2] for fluorine-containing compounds have usually been examined by calculating[4] the atomic refraction of fluorine, R_{F}, and comparing it with some hypothetical norm. For this calculation, the Eisenlohr[5] increments are commonly employed. Values thus calculated for the atomic refraction of fluorine in perhalo compounds usually fall within the limits 1.05 ± 0.20, although values as low as 0.68[6] and as high as 1.61[7] have been reported. The apparent lack of consistency has been attributed for the most part to some peculiarity of fluorine and has rendered molar refractivity a rather ineffectual tool for use with perhalo compounds containing fluorine.

In the present work, the refractivity of fluorine and the other halogens in perhalo compounds is re-evaluated using the best data available and shown to give highly consistent results. The low polarizability of fluorine suggested that refractivity measurements should be particularly useful with the fluoroperhalo compounds. These substances now comprise the largest group of perhalocarbon compounds and an almost unlimited number are capable of existence.

Source and Basis for Selection of Data.—Refractivity data for a set of 112 compounds were employed in the calculations. About 70% of the data were based on new experimental work by the present authors and their co-workers in this laboratory; the remainder were taken from the literature.[8] No compound was included unless positive evidence was available establishing the purity of the sample on which density and refractive index were taken. In most cases, such data consisted of narrow boiling and, particularly, freezing ranges. For a few compounds which could not be crystallized, other criteria of purity were employed. For some compounds for which data of apparently equal reliability were available from several sources, the data were averaged.

All molar refractions cited from other sources were recalculated from the densities and refractive indices reported, using the international atomic weights of 1951[9a]; several errors in the values reported for R_{exp} were thus uncovered. Recent revisions[9b] of the atomic weights do not affect the results significantly.

In the present paper, the synthesis by unambiguous procedures of a number of fluorine-containing perhaloalkanes, mostly propanes, is reported. The physical properties of these compounds are summarized in Table I. In Table II are listed physical properties for certain of the hydrogen-containing intermediates and by-products obtained during the preparation of the compounds of Table I. Also listed in the tables are values of physical properties previously reported for these compounds.[6,7,10–33]

Two of the compounds listed in Table I are new; physical properties for the others for the most part supplement or substantially revise the earlier data. In a number of cases the validity of these revisions is supported by the best criterion of purity available for such compounds, freezing point depressions obtained from cooling curves.

Calculations of Atomic and Group Refractions

Assumptions Involved in the Computations.—In calculating any set of atomic refractions a number of

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[1] This paper was first prepared in 1957.

[2] $R_{\mathrm{exp}} = (n^2 - 1)M/(n^2 + 2)d$. The symbols employed in this paper are those of Fajans[3]; unless otherwise indicated, the symbol R stands for $R^{20}{}_{\mathrm{D}}$, the Lorentz–Lorenz molar refraction at 20° for the sodium D-line.

[3] K. Fajans, "Physical Methods of Organic Chemistry," Vol. I, part 2, 3rd Ed., A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 1169.

[4] R_{F} is obtained by subtracting from R_{exp} the Eisenlohr increments[5] for all other atoms, exaltations, etc., and then dividing by the number of fluorine atoms in the molecule.

[5] F. Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1910); for the sodium D-line, the increments are C, 2.418; H, 1.100; Br, 8.865; Cl, 5.967; I, 13.900; double bond, 1.733.

[6] E. G. Locke, W. R. Brode, and A. L. Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934).

[7] A. L. Henne, A. M. Whaley, and J. K. Stevenson, *ibid.*, **63**, 3478 (1941).

[8] The literature search covered C_1–C_6 fluorine-containing perhalocarbons through June 1963 (*Chem. Abstr.*, **58**).

[9] (a) E. Wichters, *J. Am. Chem. Soc.*, **74**, 2447 (1952); (b) A. E. Cameron and E. Wichters, *ibid.*, **84**, 4175 (1962).

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[24] A. L. Henne and M. W. Renoll, *ibid.*, **61**, 2489 (1939).

[25] A. L. Henne and F. W. Haeckl, *ibid.*, **63**, 3476 (1941).

[26] A. L. Henne, "Organic Chemistry," Vol. I, H. Gilman, Ed., 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 956.

[27] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 257.

[28] A. Turkevich and C. P. Smyth, *J. Am. Chem. Soc.*, **62**, 2468 (1940).

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[31] A. L. Henne and E. P. Plueddeman, *ibid.*, **65**, 1271 (1943).

[32] F. K. Beilstein, "Handbuch der Organischen Chemie," 4th Ed., Vol. I, 1919, p. 106.

[33] E. H. Huntress and F. Sanchez-Nieva, *J. Am. Chem. Soc.*, **70**, 2813 (1948).

TABLE I

PHYSICAL PROPERTIES OF PERHALOETHANES AND -PROPANES[a]

No.	Compd.	Ref.	B.p.[b] (760 mm.), °C.	B.p. range, °C.	F.p.,[c] °C.	F.p. dep.,[d] °C.	$n^{20}D$	d^{20}_4	R_{exp}
I	CCl_2FCClF_2		47.7	<0.1	−36.8	0.2	1.3588	1.5748	26.18
		e	47.7		−36.4		1.3580^f	1.5754^f	26.12
II	CCl_3CF_3		46.4	0.2	14.2	0.1	1.3603	1.5772	26.24
		g	45.9^h		14.2		1.3610	1.5790	26.26
VI	$CCl_3CF_2CCl_3$		196.1	<0.1	−4.2	0.4	1.4791	1.8023	45.13
		i	194.2		−12.9		1.47996	1.8105	44.99
		j	$196.5–197.0^h$	0.5	−5		1.4777^k	1.7975^k	45.11^l
VII	$CCl_3CF_2CCl_2F$		155.4	0.1	−85.4	<0.1	1.4389	1.7549	40.51
		m	154.5		$<-80^n$		1.43939	1.7590	40.45
VIII	$CCl_2FCF_2CCl_2F$		114.8	0.1	−97.6	<0.1	1.3959	1.7021	35.83
IX	$CCl_2FCF_2CClF_2$		75.0	<0.1	−132.4	<0.1	1.3512	1.6454^o	31.14
		j	$72–73^h$	1	...		1.3578^k	1.6429^k	31.70^l
X	$CClF_2CF_2CClF_2$		36.1	<0.1	−124.9	<0.1	1.3027	1.5744	26.46
		p	$35.7^{h,q}$		-125.8^q				
		r	35.7^h		...		1.3033^f	1.5705^f	26.57
		s	35.8^h		...		1.3030	1.5730	26.51
XI	$CCl_3CF_2CClF_2$		113.9	0.1	−92.3	0.2	1.3969	1.7034	35.88
		t	113.95		−92.78	0.1	1.3966	1.7034	35.86
XVIa	$CCl_3CClFCCl_3$		140.8 (50 mm.)		9.6	1.1	1.5198	1.8521	49.76
XVIb			140.8 (50 mm.)		9.8	0.7	1.5198	1.8520	49.76
		u	105 (15 mm.)		8.4	0.8	1.5194	1.8515	49.74^v
XXI	$CCl_2FCClFCCl_2F$		153.9	0.2	−88.5	<0.1	1.4378	1.7606	40.29
		w	154.7		Glass		1.4387	1.7624	40.32
XXII	$CCl_2FCClFCClF_2{}^x$		113.8	<0.1	Glass at − 150°		1.3958	1.7121	35.61
XXIII	$CClF_2CClFCClF_2$		74.0	0.1	−135.4	<0.1	1.3504	1.6525	30.94
		y	73.9	0.1	α −141.3 β −135.0	<0.1	1.3501	1.6541	30.89
		z	73.8	<0.1	α −141.5 β −134.7	<0.1	1.3502	1.6540	30.90
XXIV	$CClF_2CClFCF_3$		34.8	<0.1	−131.1	0.3	1.3034	1.5903	26.25
		aa	34.7^h		−136	1.0	1.3029	1.5896	26.22
		p	34.5^h		−132.7				
XXV	$CCl_3CClFCCl_2F$		124.0 (100 mm.)		*ca.* -55^{bb}		1.4794	1.8043	45.10
		t	196.0		−55	0.5	1.4791	1.8080	44.99
XXVI	$CF_3CClFCF_3$		−2.2	<0.1	−86.6	1.8			
		aa	−2		Glass				
XXVII	$CCl_3CCl_2CF_3$		153.0	<0.1	108.2	0.2			
		cc	153.1^h		109.1				
XXVIII	$CClF_2CCl_2CF_3$		72.0	<0.1	−4.5	0.3	1.3518	1.6667^{dd}	30.79
		cc	72.0		−4.30		1.3519	1.6681	30.77
XXIX	$CCl_3CCl_2CClF_2$		194.6	<0.2	55.5	1.0			
		i, ee	193.4^h		50.8				
XXX	$CClF_2CCl_2CClF_2$		112.3	<0.1	−45.9	1.7	1.3960	1.7184	35.50
		ff	112.0^h		−42.9		1.39584	1.7199	35.45
XXXI	$CCl_2FCCl_2CClF_2$		153.2	<0.1	−3.9	0.4	1.4392	1.7694	40.20
		i, ff	152.3^h		−4.9		1.43959	1.77023	40.21

[a] The values given in the upper line were found in this work; those given in the lower lines are from the references cited. [b] See Experimental for method of correcting observed boiling point to 760 mm. [c] Maximum equilibrium temperature attained from cooling or warming curve; see Experimental. [d] Freezing point depression with the material estimated to be half frozen. [e] Ref. 6. [f] Calculated from data reported at other temperatures. [g] Ref. 10. [h] Pressure not stated. [i] Ref. 11. [j] Ref. 12. [k] At 25.0°. [l] Corrected to 20°; see text. [m] Ref. 13. [n] F.p. −89°.[26] [o] d^{20}_4 1.6229. [p] Ref. 14. [q] Average of two values obtained on different samples. [r] Ref. 15. [s] Ref. 16. [t] Ref. 17. [u] Ref. 18. [v] Reported[18] 49.93; recalculation gave 49.74. [w] Ref. 19. [x] Henne and Haeckl[25] have reported this compound; however, their identification is questionable; see Experimental. [y] Ref. 20. [z] Ref. 21. [aa] Ref. 22. [bb] It was found difficult to obtain a good cooling curve, because of the slow rate of crystal growth. [cc] Ref. 7. [dd] d^{20}_4 1.6443. [ee] Ref. 23. [ff] Ref. 24.

more or less arbitrary assumptions must be made. In the calculations which follow, most of these assumptions are explicitly stated. The most important ones employed in the present work are (a) that the atomic refraction of carbon in perhalo compounds is identical with that in hydrocarbons, and (b) that the atomic refraction of fluorine bonded to carbon is invariant with position. Other assumptions might have been made, and a different set of refractions thus obtained. The necessarily arbitrary nature of the atomic refractions herein proposed should thus be recognized.

In the present work, the approach has been to minimize the difference between R_{exp} and R_{add}, rather than the per cent difference between the two.

Temperature Dependence of Molar Refraction.—Organic liquids are known[3] to show increases in R_{exp} of 0.005–0.02%/deg. An average value for five perhalo compounds[34] is +0.015 ± 0.003%/deg.; this figure is tentatively suggested for correcting molar re-

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(34) CCl_4, +0.018; $CBrCl_3$, +0.012; C_2Cl_4, +0.012; CCl_2FCClF_2, +0.038 (omitted from average); CCl_2FCCl_2F, +0.019; and n-C_7F_{16}, +0.013% deg.

TABLE II

PHYSICAL PROPERTIES OF HYDROGEN-CONTAINING INTERMEDIATES[a]

No.	Compd.	Ref.	B.p.[b] (760 mm.), °C.	B.p. range, °C.	F.p.,[c] °C.	F.p. dep.,[d] °C.	n^{20}_D	d^{20}_4	R_{exp}
III	$CH_3CCl_2CH_3$		69.5	<0.1	−33.9	<0.1	1.4149	1.0914	25.90
		e	70.5		−34.4		1.4153[f]	1.0915[g]	25.92
		h	69.3	<0.1	−33.8				
IV	$CH_2ClCHClCH_3$		96.5	<0.1	−100.3	<0.1	1.4392	1.1565	25.69
		i	96.20		−100.42		1.43901	1.15577	25.70
V	$CH_3CClFCH_3$		35.6	0.4	−93.2	0.2	1.3521	0.9975	20.94
		j	35.2		...		1.35856[k]	1.0072[k]	21.10[l]
XII	$CH_2{=}CClCH_2Cl$		93.7	0.2	α −90.0 β −83.1	1.0	1.4592	1.2039	25.23
		m	93.6	0.1	...		1.4609	1.2150	25.06
XIII	$CH_2ClCF_2CH_3$		55.9	<0.1	−56.8	0.4	1.3522	1.1935	20.76
		n	55.1[o]	0.2	−56.2		1.3520	1.2001	20.64
XIV	$CH_2ClCClFCH_3$		88.6	<0.1	α −91.3 β −88.8	<0.1	1.4099	1.2622	25.71
		p	88.6[o]		−91.7		1.4099	1.2624	25.70
XV	$CH_2ClCCl_2CH_3$		122.6	0.1	−65.9	0.2	1.4618	1.3233	30.62
		q, r	123				1.4609[s]	1.324[q]	
XVII	$CHCl_2CClFCH_3$		116.9	0.4	Glass at −120°		1.4360	1.4223	30.41
		n	116.7[o]		Glass		1.4360	1.4238	30.38
XVIII	$CCl_3CClFCH_3$		139.7	<0.1	102.4	2.4			
		n	139.6[o]		104.5	0.5			
XIX	$CHCl_2CClFCH_2Cl$		160.9	0.2	Glass at −100°		1.4682	1.5844	35.08
		n	50–51 (14 mm.)		Glass		1.4694	1.5782	35.30
XX	$CCl_3CClFCH_2Cl$		101.5 (50 mm.)		−39.1	Large	1.4871	1.6839	40.03
		n	72 (14 mm.)		−34.4		1.4871	1.6867	39.96[t]

[a] The values given in the upper line were found in this work; those given in the lower lines are from the references cited. [b] See Experimental for method of correcting observed boiling points to 760 mm. [c] Maximum equilibrium temperature attained from cooling or warming curve; see Experimental. [d] Freezing point depression with material estimated to be half frozen. [e] Ref. 27. [f] Interpolated from data reported[27] for the H_α- and H_β-lines with the relation[35] $n_D = n_{H\alpha} + 0.29(n_{H\beta} - n_{H\alpha})$. [g] Interpolated from data reported at other temperatures. [h] Ref. 28. [i] Ref. 29. [j] Ref. 13. [k] At 10.0°. [l] Corrected to 20.0°; see text. [m] Ref. 30. [n] Ref. 18. [o] Pressure not reported. [p] Ref. 31. [q] Ref. 32. [r] Ref. 33. [s] At 25.0°. [t] Reported[18] 39.37; recalculation gave 39.96.

fractions for perhalo compounds to 20.0°. Over the range 0–40°, the error arising from the uncertainty in the magnitude of the correction would appear to be less than 0.1% of R_{exp}.

Atomic Refraction of Carbon and Fluorine Perfluoro-*n*-alkanes.—Ideally, the atomic refractions for carbon and fluorine should be calculated from data on the perfluoro-*n*-alkanes, independently of other series of compounds. Thus, there is no *a priori* reason to expect that the atomic refraction of carbon in perfluoro compounds should be identical with that in hydrocarbons; on the contrary, some difference would be expected. Unfortunately, at present acceptable data are available for only two of the five[36] liquid perfluoro-*n*-alkanes: (1) perfluoropentane,[40,41] R^{15}_{exp} 26.884, R^{20} 26.903[42]; and (2) perfluoroheptane,[43] R^{20}_{exp} 36.726, R^{30}_{exp} 36.774. While these data are sufficient to yield the values $R_C = 2.566$ and $R_F = 1.173$, a small change in R_{exp} for either compound would produce a large change in the atomic refractions of both elements. In view of this uncertainty, we do not feel justified in proposing these values at present.

In the present work, R_C was obtained from the set of selected values of the American Petroleum Institute[44] for the *n*-alkanes, C_5H_{12} to $C_{16}H_{34}$. For this set, the least-squares value[45] for CH_2 is 4.6424 and for H is 1.0277. Inasmuch as the uncertainty in these values is of the order of 0.001, there is at present no justification for retaining the fourth decimal place. On rounding off the value for CH_2 to 4.642, it was found that the data for the *n*-alkanes is best fitted by the value for H of 1.029. These values reproduce the molar refractions for the 12 *n*-alkanes, C_5H_{12} to $C_{16}H_{34}$, with a probable error[47] in R_{add} of 0.003, and an average deviation of ±0.008%.

With the assumption that R_H in CH_2 has the same value that it has in CH_3, $R_C = R_{CH_2} - 2R_H = 2.584$. Using this value for carbon, and, with the assumption

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(35) H. Waldmann, *Helv. Chim. Acta*, **21**, 1053 (1938).

(36) Styles and Cady's[37] *n*-C_6F_{14} "may have contained up to 4.5 mole % of impurity." Brice and Coon[38] reported physical properties for *n*-C_6F_{14} and *n*-C_8F_{18}, but gave no evidence for the purity of their preparations. Density and refractive indices reported by Haszeldine and Smith[39] for *n*-C_8F_{18} and *n*-C_9F_{20} were given to only three places. *n*-$C_{10}F_{22}$ and higher perfluoro-*n*-alkanes melt well above 20°.[39]

(37) V. E. Styles and G. H. Cady, *J. Am. Chem. Soc.*, **74**, 3771 (1952).

(38) T. J. Brice and R. I. Coon, *ibid.*, **75**, 2921 (1953).

(39) R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 3617 (1950).

(40) G. H. Rohrbach and G. H. Cady, *J. Am. Chem. Soc.*, **71**, 1938 (1949).

(41) L. L. Burger and G. H. Cady, *ibid.*, **73**, 4243 (1951).

(42) Calculated from the data at 15° on the basis that the temperature dependence for perfluoropentane is the same as that found for perfluoroheptane, +0.013%/deg.

(43) G. D. Oliver, *et al.*, *J. Am. Chem. Soc.*, **73**, 5722 (1951).

(44) American Petroleum Institute, "Selected Values of Properties of Hydrocarbons and Related Compounds," Research Project 44, 1956, Tables 20a and 20b.

(45) Van der Hulst[46] has pointed out that the mathematically correct treatment of the data requires the use of the method of least squares.

(46) L. J. N. Van der Hulst, *Rec. trav. chim.*, **54**, 518 (1935).

(47) The probable error,[48] *r*, is calculated with the equation

$$r = 0.6745\sqrt{\sum_{i=1,\ldots,n} (d_i^{\,2})/(n-f)}$$

where *d* is the difference between the experimental and calculated values *n* is the number of pieces of data, and *f* is the number of disposable parameters calculated from the set of data.

(48) (a) A. H. Margenau and G. M. Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 502; (b) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 12, 15.

TABLE III

ATOMIC REFRACTION OF TERMINAL CHLORINE IN PERHALO-*n*-ALKANES

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	No. of Cl atoms	R_{Cl} (terminal)[a]	R_{add} (Table XII)
3a	*b*	CCl_3CF_3		26.241			
3b	*c*	CCl_3CF_3		26.257			
3c		CCl_3CF_3	26.46	26.249 (av.)	3	5.862	26.21
4	*b*	CCl_2FCClF_2	26.46	26.182	3	5.840	26.21
5a	*d*	CCl_2FCCl_2F		30.881[e]			
5b	*f*	CCl_2FCCl_2F		30.877[e]			
5c			31.18	30.879 (av.)	4	5.845	30.90
6	*b*	$CClF_2CF_2CClF_2$	26.63	26.458	2	5.858	26.44
7	*b*	$CCl_2FCF_2CClF_2$	31.26	31.141	3	5.855	31.13
8a	*b*	$CCl_3CF_2CClF_2$		35.881			
8b	*g*	$CCl_3CF_2CClF_2$		35.857			
8c		$CCl_3CF_2CClF_2$	36.08	35.869 (av.)	4	5.864	35.81
9	*b*	$CCl_2FCF_2CCl_2F$	36.08	35.828	4	5.854	35.81
10	*b*	$CCl_3CF_2CCl_2F$	40.81	40.507	5	5.852	40.50
11	*b*	$CCl_3CF_2CCl_3$	45.54	45.128	6	5.841	45.18
12	*h*	$CCl_3CF_2CF_2CCl_3$	50.43	50.059	6	5.844	50.10
				Weighted average for terminal Cl		5.850 ± 0.007	

[a] Calculated by subtracting from R_{exp} the atomic refractions for carbon and fluorine (Table XII) and then dividing by the number of chlorine atoms. [b] Ref. 49. [c] Ref. 10. [d] Ref. 50. [e] Corrected to 20.0°; see text. [f] Ref. 6. [g] Ref. 17. [h] Ref. 51.

that R_F is the same in CF_2 and CF_3, the data for perfluoropentane and perfluoroheptane yield $R_F = 1.165$.

In all succeeding calculations, the atomic refraction of fluorine bonded to carbon in perhalo compounds is *assumed to be invariant* and equal to 1.165. This assumption is justified on the following grounds. As will be shown below, some of the halogens *must* be multivalued in order to fit the experimental data. The much more polarizable chlorine, bromine, and iodine atoms should vary in value with position more than fluorine. For convenience, *all* of the variation will be attributed to chlorine, bromine, and iodine. This procedure turns out to minimize the number of parameters required to fit the data, and this provides additional justification for its use.

Atomic Refraction of Chlorine in the Terminal Position in Perhalo-*n*-alkanes.—Trial calculations with the chlorofluoroalkanes indicated a marked difference in the atomic refraction of chlorine in the terminal and internal positions. Molar refractions for pure compounds[6,10,17,49–51] containing chlorine in the terminal position only are listed in Table III.

Initially, estimates were made of the group refractions for CCl_3, CCl_2F, and $CClF_2$. Compounds **3c**, **11**, and **12** yielded for CCl_3 20.12 ± 0.02; compounds **5c** and **9** yielded for CCl_2F 15.45 ± 0.01; and compound **6** yielded for $CClF_2$ 10.77. These group refractions fit the data for the other four compounds in Table III quite accurately. Assuming that the atomic refractions of carbon and fluorine are invariant in these groups and equal to 2.584 and 1.165, respectively, the atomic refraction of chlorine in CCl_3, CCl_2F, and $CClF_2$ is 5.84, 5.85, and 5.86, respectively. This result justifies expressing the data in terms of a single value for R_{Cl} (terminal), 5.850 ± 0.007, the weighted average for 40 terminal chlorine atoms.

The Eisenlohr values[52] fit the molar refractions found for the ten compounds of Table III with a probable error[57a] in R_{add} of 0.19. An eightfold improvement in the fit is obtained for this set of compounds when the atomic refractions proposed above are employed; the probable error[57b] in R_{add} is reduced to 0.024.

Atomic Refraction of Chlorine in Internal Positions in Perhalo-*n*-alkanes.—Table IV lists molar refractions found for 20 pure compounds containing chlorine in both terminal and internal positions.[7,11,17,19–21,24,25,49–51,58–62] It would be desirable to evaluate the atomic refraction for internal chlorine independently of that for terminal chlorine, in order to check on group interactions. This, however, is not possible at present. The procedure employed, therefore, was to assume such interactions are negligible, and to use the value calculated above for terminal chlorine.

In this way, compounds **13** through **23** give for CClF 9.43 ± 0.03, and compounds **24** through **32** give for CCl_2 13.974 ± 0.029. Assuming, as before, the atomic refractions of carbon and fluorine are invariant in these groups, and equal to 2.584 and 1.165, respectively, the atomic refraction of chlorine in CClF and CCl_2 is 5.68 ± 0.03 and 5.695 ± 0.015, respectively. Again, since those values overlap, the data can be expressed more simply in terms of a single value for R_{Cl} (internal) of 5.69 ± 0.02, the weighted average for 38 internal chlorine atoms. This value is sufficiently different from that for terminal chlorine, 5.850 ± 0.007, to justify employing two separate values instead of a single average value.

The Eisenlohr values fit R_{exp} for the 20 compounds of Table IV with a probable error[57a] in R_{add} of 0.42.

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(49) Reported in this paper.

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(51) A. L. Henne, J. B. Hinkamp, and W. J. Zimmerschied, *J. Am. Chem. Soc.*, **67**, 1906 (1945).

(52) Eisenlohr[5] did not list a value for the atomic refraction of fluorine. Using his value for carbon, 2.418, the data on perfluoropentane and perfluoroheptane yield a value for $R_F = 1.24$. This value, ±0.02, has been employed by other investigators.[53–56]

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(57) (a) $f = 0$; (b) $f = 1$; (c) $f = 2$; see ref. 47.

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TABLE IV

ATOMIC REFRACTION OF INTERNAL CHLORINE IN PERHALO-*n*-ALKANES

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	R_{CClX}[a]	R_{Cl} (internal)[b]	R_{add} (Table XII)
13		$CClF_2CClFCF_3$	26.63	26.249	9.406	5.657	26.28
14	*d*	$CCl_2FCClFCF_3$	31.36	30.947	9.416	5.670	30.97
15a	*c*	$CClF_2CClFCClF_2$		30.944			
15b	*d*	$CClF_2CClFCClF_2$		30.890			
15c	*e*	$CClF_2CClFCClF_2$		30.900			
15d		$CClF_2CClFCClF_2$	31.36	30.911 (av.)	9.386	5.627	30.97
16	*c*	$CCl_2FCClFCClF_2$	36.08	35.611	9.398	5.649	35.65
17	*f, g*	$CCl_3CClFCF_3$	36.08	35.684	9.471	5.722	35.65
18	*c*	$CCl_2FCClFCCl_2F$	40.81	40.288	9.390	5.641	40.34
19a	*c*	$CCl_3CClFCCl_2F$		45.102			
19b	*h*	$CCl_3CClFCCl_2F$		44.986			
19c		$CCl_3CClFCCl_2F$	45.54	45.044 (av.)	9.461	5.712	45.02
20	*c*	$CCl_3CClFCCl_3$	50.26	49.758	9.490	5.741	49.71
21	*i*	$CF_3CClFCClFCF_3$	31.53	31.078	9.460	5.711	31.04
22	*j*	$CClF_2CClFCClFCClF_2$	40.98	40.392	9.432	5.683	40.41
23	*e*	$(CClF_2CClFCF_2-)_2$	50.78	50.175	9.410	5.661	50.23
				Weighted average for R_{CCF}	9.430 ± 0.028		
24a	*c*	$CClF_2CCl_2CF_3$		30.791			
24b	*f*	$CClF_2CCl_2CF_3$		30.773			
24c		$CClF_2CCl_2CF_3$	31.36	30.782 (av.)	13.939	5.677	30.81
25	*c*	$CClF_2CCl_2CClF_2$	36.08	35.496	13.968	5.692	35.49
26a	*c*	$CCl_2FCCl_2CClF_2$		40.200			
26b	*k, l*	$CCl_2FCCl_2CClF_2$		40.212			
26c		$CCl_2FCCl_2CClF_2$	40.81	40.206 (av.)	13.993	5.705	40.18
27	*k*	$CCl_2FCCl_2CCl_2F$	45.54	44.899[m]	14.001	5.712	44.86
28	*n*	$CCl_3CF_2CCl_2CF_3$	45.71	44.968	13.841	5.629	45.09
29	*o*	$CClF_2CCl_2CCl_2CClF_2$	50.43	49.524	13.998	5.707	49.46
30	*o*	$CCl_2FCCl_2CCl_2CClF_2$	55.16	54.236	14.011	5.714	54.14
31	*p*	$CCl_3CF_2CCl_2CCl_3$	59.89	59.165	13.983	5.700	59.15
32	*q*	$CCl_2FCCl_2CCl_2CCl_2F$	59.89	58.844	13.973	5.695	58.83
				Weighted average for R_{CCl_2}	13.974 ± 0.029		
					Weighted average for R_{Cl} (internal)	5.690 ± 0.023	

[a] X = F for compounds **13–23**, X = Cl for compounds **24–32**; R_{CClX} was obtained by subtracting from R_{exp} the values for halogen and carbon in the terminal groups, Table XII, and then dividing by the number of CClX groups. [b] Obtained by subtracting from R_{exp} the values for carbon, fluorine, and chlorine (Table XII), and then dividing by the number of internal chlorine atoms. [c] Ref. 49. [d] Ref. 20. [e] Ref. 21. [f] Ref. 7. [g] Ref. 25. [h] Ref. 17. [i] Ref. 19. [j] Ref. 50. [k] Ref. 11. [l] Ref. 24. [m] Corrected to 20.0°, see text. [n] Ref. 51. [o] Ref. 58 and 59. [p] Ref. 60. [q] Ref. 61.

The present values reduce the probable error[57b] to 0.035.

Atomic Refraction of Terminal and Internal Bromine in Perhalo-*n*-alkanes.—Table V lists molar refractions found for 17 pure bromine-containing perhalo-*n*-alkanes.[20,21,60–64] Utilizing the atomic refractions calculated above for carbon, fluorine, and terminal and internal chlorine, the data of Table V are best fitted by using two values for the atomic refraction of bromine, corresponding to the terminal and internal positions.

Thus, compounds **33–36** yield a group refraction for $CBrF_2$ of 13.45 ± 0.03. Using this value, compounds **37–41** give for CBrClF 18.22 ± 0.07. With the assumptions stated above, these group refractions yield for bromine atomic refractions of 8.54 ± 0.03 and 8.62 ± 0.07. As before, this overlap justifies employing a single value for R_{Br} (terminal) of 8.57 ± 0.06, the weighted average for 12 terminal bromine atoms.

Assuming this value for terminal bromine, together with the values already determined for the other elements, compounds **42–45** give for CBrF 11.90 ± 0.2, and compounds **46–49** give for CBrCl 16.49 ± 0.02; these give for internal bromine 8.15 ± 0.02 and 8.21 ± 0.02, respectively. While a slightly better fit is obtained by using separate values, this gain is *at present* not considered sufficient to outweigh the advantage of a single value for R_{Br} (internal), 8.18 ± 0.03, the average for eight internal bromine atoms.

The Eisenlohr values fit the molar refractions for the 17 compounds of Table V with a probable error[57a] in R_{add} of 0.54. The values derived above reduce the probable error[57c] to 0.043.

Atomic Refraction of Terminal and Internal Iodine in Perhalo-*n*-alkanes.—Acceptable refractivity data are at present available for only five iodine-containing perhaloalkanes[63,65–68]; these are listed in Table VI. Compounds **50**, **52**, and **53** give for R_{I} (terminal) 13.73 ± 0.03, the weighted average for five iodine atoms. However, compound **52** yields the value 13.32, far out of line. The reason for this discrepancy remains to be determined. It may turn out that the data for this or the other compounds are in error, or that nonbonded

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TABLE V

ATOMIC REFRACTION OF TERMINAL AND INTERNAL BROMINE IN PERHALO-*n*-ALKANES

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	Group refraction[a,b]	R_{Br}[b]	R_{add} (Table XII)
33	*c*	$\mathrm{CBrF_2CClF_2}$	24.63	24.21_3	13.45	8.53_5	24.25
34a	*c*	$\mathrm{CBrF_2CBrF_2}$		26.98_3			
34b	*d*	$\mathrm{CBrF_2CBrF_2}$		26.97_1			
34c		$\mathrm{CBrF_2CBrF_2}$	27.53	26.97_7 (av.)	13.49	8.57_5	26.97
35	*e*	$\mathrm{ClBrF_2CClFCClF_2}$	34.25	33.58_5	13.38	8.46_8	33.69
36	*e*	$\mathrm{ClBrF_2CClFCBrF_2}$	37.15	36.32_4	13.44	8.52_8	36.41
37	*f*	$\mathrm{CBrClFCBrF_2}$	32.25	31.61_2	18.16	8.54_9	31.65
38	*d*	$\mathrm{CBrClFCF_2CCl_2F}$	38.98	38.64_7	18.28	8.68_9	38.53
39	*d*	$\mathrm{CBrClFC_2CCl_3}$	43.71	43.15_5	18.11	8.50_8	43.22
40	*d*	$\mathrm{CBrClFCClFCCl_3}$	48.43	47.88_3	18.31	8.71_1	47.74
41	*d*	$\mathrm{CBrClFCF_2CClFCF_2CCl_3}$	58.23	57.63_2	18.23	8.63_2	57.57
				Weighted average for R_{Br} (terminal)		$8.57_1 \pm 0.05_5$	
42	*g*	$\mathrm{CBrF_2CBrFCClF_2}$	37.15	36.15_4	11.90_6	8.15_7	36.19
43	*c*	$\mathrm{CBrF_2CBrFCF_3}$	32.42	31.44_9	11.88_6	8.13_7	31.50
44	*e*	$\mathrm{CBrF_2CBrFCBrF_2}$	40.05	38.85_6	11.88_8	8.13_9	38.91
45	*c*	$\mathrm{CBrClFCBrFCClF_2}$	41.88	40.90_3	11.93_0	8.22_1	40.87
46	*d*	$\mathrm{CBrF_2CBrClCF_3}$	37.15	36.06_6	16.50_3	8.22_9	36.03
47	*g*	$\mathrm{CBrF_2CBrClCClF_2}$	41.88	40.74_8	$16\ 50_0$	8.22_6	40.71
48	*e*	$\mathrm{CBrF_2CBrClCBrF_2}$	44.78	43.44_4	16.47_6	8.20_2	43.43
49	*d*	$\mathrm{CF_3CBrClCF_2CCl_3}$	48.60	47.58_7	16.46_0	8.18_6	47.59
				Average for R_{Br} (internal)		$8.18_7 \pm 0.03_2$	

[a] $R_{\mathrm{CBrF_2}}$ for compounds **33–36**; R_{BrClF} for **37–41**; R_{BrF} for **42–45**; R_{BrCl} for **46–49**. [b] Obtained by subtracting from R_{exp} the refractions for atoms or groups previously found, and then dividing by the proper number. [c] Ref. 62. [d] Ref. 63. [e] Ref. 21. [f] Ref. 64. [g] Ref. 20.

TABLE VI

ATOMIC REFRACTION OF TERMINAL AND INTERNAL IODINE IN PERHALO-*n*-ALKANES

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	R_{I}[a]	R_{add} (Table XII)
50	*b*	$\mathrm{CClFICF_2CCl_3}$	48.74	48.43_6	13.78_9	48.38
51	*c*	$\mathrm{CF_2ICF_2CF_2I}$	42.49	42.17_8	13.71_8	42.20
52	*d*	$\mathrm{CF_3CF_2CF_2I}$	29.83	29.20_4	13.297[e]	29.64
53	*f*	$\mathrm{(CF_2ICF_2)_2}$	47.39	47.06_5	13.70_5	47.12
		Weighted average[e] for terminal iodine			$13.7_3 \pm 0.0_3$	
54	*g*	$\mathrm{CF_3CFICF_3}$	29.83	29.62_8	12.72_1	*h*

[a] Obtained by subtracting from R_{exp} the values for carbon, fluorine, and terminal chlorine (Table XII), and dividing by the number of iodine atoms. [b] Ref. 63. [c] Ref. 65. [d] Ref. 66. [e] The value for compound **52** was omitted from the average; if it is included, $R_{\mathrm{I}} = 13.66 \pm 0.12$. [f] Ref. 67. [g] Ref. 68. [h] Used to obtain the atomic refraction of internal iodine.

interactions play a sufficiently more important role for perhalogenated iodides than for chlorides and bromides to require special treatment. Until this point is settled, however, the value for terminal iodine must be considered somewhat uncertain and is expressed as 13.7_3.

Compound **54** gives a value of 12.7 for internal iodine.

Perhalocyclobutanes.—Molar refractions found for the four perhalocyclobutanes for which such data[50,62,69–71] are at present available are listed in Table VII. Assuming that the atomic refractions for carbon[73] and fluorine are the same in these compounds as in the perhalo-*n*-alkanes, the atomic refractions for chlorine and bromine, and the C_4 ring increment were calculated as follows. The difference between R_{exp} for compounds **55** and **56** is $\mathrm{R_{Cl} - R_F}$; the same is true for the pair **57** and **58**. These yield for R_{Cl} in perhalocyclobutanes 5.899 ± 0.003. In a similar fashion, the

TABLE VII

MOLAR REFRACTION OF PERHALOCYCLOBUTANES AND PERHALOCYCLOBUTENES

No.	Ref.	Compd.	R_{add} (Eisenlohr)[a]	R_{exp}	R_{add} (Table XII)
55	*b*	$\mathrm{CClFCClFCF_2CF_2}$	29.37	22.22_9	29.23
56	*b*	$\mathrm{CClFCClFCClFCF_2}$	34.09	33.96_0	33.96
57	*c*	$\mathrm{CBrFCBrFCF_2CF_2}$	35.16	34.61_5	24.62
58	*b*	$\mathrm{CBrFCBrFCClFCF_2}$	39.89	39.35_2	39.35
59	*b*	$\mathrm{CF{=}CFCClFCF_2}$	23.57	23.46_9	23.47
60a	*b*	$\mathrm{CF{=}CFCClFCClF}$		28.32_4	
60b	*d*	$\mathrm{CF{=}CFCClFCClF}$		28.40_4	
60c	*e*	$\mathrm{CF{=}CFCClFCClF}$		28.36_0	
60d		$\mathrm{CF{=}CFCClFCClF}$	28.30	28.36_3 (av.)	28.34
61	*b*	$\mathrm{CF{=}CFCFICF_2}$	31.51	31.34_3	31.4_4
62	*e*	$\mathrm{CF{=}CFCFICFI}$	44.17	44.44_6	44.2_8
63	*e*	$\mathrm{CF{=}CFCClFCFI}$	36.23	36.27_8	36.3_1
64	*b*	$\mathrm{CF{=}CFCBrFCF_2}$	26.47	26.30_0	26.26
65	*e*	$\mathrm{CF{=}CFCBrFCBrF}$	34.09	34.00_9	33.91
66	*f*	$\mathrm{CCl{=}CClCF_2CF_2}$	28.30	28.717[g]	*h*

[a] Using 0.32 for the cyclobutane ring increment,[72] and no ring increment for the cyclobutenes. [b] Ref. 50. [c] Ref. 62. [d] Ref. 69. [e] Ref. 70. [f] Ref. 71. [g] Corrected to 20.0°; see text. [h] Employed to determine the value for CCl=CCl in cyclobutenes.

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(73) In this case, the assumption relating to the carbon value is completely arbitrary. Exactly the same result would be accomplished by splitting the ring increment between the four carbon atoms, and giving carbon a special value in perhalocyclobutanes.

TABLE VIII

MOLAR REFRACTION OF PERHALO OLEFINS WITH TERMINAL DOUBLE BOND

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	R_{add} (Table XII)
57a	*a*	$(CF_2{=}CFCF_2)_2$		30.08	
67b	*b*	$(CF_2{=}CFCF_2)_2$		30.18	
67c		$(CF_2{=}CFCF_2)_2$	30.37	30.13 (av.)	*c*
68	*a*	$(CF_2{=}CClCF_2)_2$	39.83	38.901	*c*
69	*d*	$CClF{=}CClCF_3$	25.88	25.521	*c*
70	*d*	$CCl_2{=}CFCF_3$	25.88	25.606	*c*
71	*e*	$CCl_2{=}C(CF_3)_2$	30.78	30.644	*c*
72	*f*	$CCl_2{=}CClCF_3$	30.61	30.523	30.54
73	*g*	$CCl_2{=}CClCF_2CCl_3$	49.69	49.566[h]	49.51
74	*i*	$CCl_2{=}CClCF_2CCl{=}CCl_2$	53.84	53.799	53.83
75	*f*	$CF_2{=}CClCClF_2$	25.88	25.458	25.48
76	*d*	$CCl_2{=}CFCCl_3$	40.06	40.218	40.20
77	*f*	$CCl_2{=}CClCClF_2$	35.19	35.509	35.40
78	*f*	$CCl_2{=}CClCCl_2F$	40.06	40.375	40.27
79	*f*	$CCl_2{=}CClCCl_3$	44.79	44.914	45.13
80	*j*	$CCl_2{=}CClCCl_2CClF_2$	49.69	49.294	*c*
81	*a*	$CF_2{=}CClCBrF_2$	28.78	28.307	28.27
82	*a*	$CF_2{=}CFCBrF_2$	24.05	23 856	23.88
83	*f*	$CF_2{=}CClCF_2I$	33.81	33.592	33.45
84	*f*	$CF_2{=}CFCF_2I$	29.09	28.897	29.06

[a] Ref. 21. [b] Ref. 74. [c] Employed to determine atomic or group refraction. [d] Ref. 22. [e] Ref. 75. [f] Ref. 20. [g] Ref. 76. [h] Corrected to 20.0°; see text. [i] Ref. 78. [j] Ref. 71.

difference between **55** and **57** is equal to 2 ($R_{Br} - R_{Cl}$); another such difference is obtained from **56** and **58**. Using the value for chlorine determined above (5.899), these differences give for R_{Br} in perhalocyclobutanes, 8.593 ± 0.003. These values for chlorine and bromine in perhalocyclobutanes differ sufficiently from those previously found for these elements in both the internal and terminal positions to warrant employing them as separate values. Using them, the C_4 ring increment is found to be +0.104 ± 0.002.

Utilizing four pieces of data to set the values for three disposable parameters leaves but one compound to check on the set. This one check is almost perfect, but is not considered adequate to warrant retaining the third decimal place, which is rounded off in the final tabulation. Additional data are, of course, desirable.

Perhalo Olefins with Terminal Double Bonds.—In general, the refraction increment for the double bond may be expected to vary with the nature of the substituents on the vinyl carbon atoms. For this reason, terminally and internally unsaturated perhalo olefins will be considered separately. Molar refractions found for the former are listed in Table VIII. See ref. 20–22, 71, and 74–78.

Allylic exaltations may be expected for the halogens.[79] It is necessary to assume that the allylic exaltation for fluorine is negligible; otherwise the exaltations for the other halogens could not at present be separated from the unsaturated group increments. With this assumption, compounds **67–74** yield the following group refractions: $CF_2{=}CF$, 10.15; $CF_2{=}CCl$, 14.54; $CClF{=}CCl$,[81] 19.44; $CCl_2{=}C<$, 18.49; $CCl_2{=}CF$, 19.53; and $CCl_2{=}CCl$, 24.46 ± 0.03. Of necessity, all but one of these values is based on data for single compounds; the values may therefore be expected to undergo some revision as more data become available.

Using these unsaturated group refractions, compounds **75–79** give for R_{Cl} (terminal allylic) 6.03 ± 0.05[82]; compound **80** gives 5.74 for R_{Cl} (internal allylic); compounds **81** and **82** give 8.82 ± 0.03 for R_{Br} (terminal allylic); and compounds **83** and **84** give 14.0 ± 0.15 for R_I (terminal allylic). These values all clearly demonstrate the reality of the allylic exaltation.

The Eisenlohr increments fit the molar refractions found for the 18 olefins of Table VIII with a probable error[57a] in R_{add} of 0.23. The data of Table VIII were used to determine 10 parameters; the probable error[83] in R_{add} for the fit resulting from the use of these parameters is 0.086.

This fit is not nearly so good as that obtained for the saturated compounds. At least two factors may be responsible: (1) compared with the perhaloalkanes the olefins are known to be more difficult to obtain and retain in a highly pure state; *i.e.*, the experimental data for the perhalo olefins may be poorer; and (2) it may prove necessary to take account of additional interactions between nonbonded atoms; *e.g.*, see ref. 82. There is reason to feel, however, that the fit can be substantially improved when more and better data become available.

Perhalo Olefins with Internal Double Bonds.—All of the open-chain perhalo olefins with internal double bonds for which adequate data are available, see Table IX, exist as *cis–trans* isomers which can be expected to have appreciably different refractions. Inasmuch as no data on configuration are available for any of these compounds, refractivity values for those which are reported to freeze sharply cannot be considered appreciably superior for the present purposes to those for which no such criterion of purity is reported. For this reason, all of the pertinent compounds for which molar refractions are available, listed in Table IX, will be treated together.

Using the values previously calculated for the allylic halogens, compounds **85–87** give for $CCl{=}CCl$[84] 18.50 ± 0.06, while compound **88** gives for the same group 17.43; compounds **89** and **91** give for $CCl{=}CF$ 13.60 ± 0.02, while compound **90** gives 13.11; compounds **92–96** give for $CF{=}CF$ values ranging from 8.57 to 9.35, averaging 9.0 ± 0.2.

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(74) W. L. Thompson, Ph.D. Thesis, Cornell University, 1955.

(75) A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950).

(76) T. Newby, M.A. Thesis, The Ohio State University, 1944; cited by Henne.[77]

(77) A. L. Henne, *J. Am. Chem. Soc.*, **75**, 5750 (1953).

(78) A. L. Henne and E. G. DeWitt, *ibid.*, **70**, 1549 (1948).

(79) Koutecky[80] gives exaltations of +0.4 for Cl and +0.8 for Br in the allylic position in hydrogen-containing compounds.

(80) J. Koutecky, *Chem. Listy*, **38**, 10 (1944).

(81) This group exists in the *cis* and *trans* forms. These two forms will, in general, have different refractions. Thus, for instance, *cis-* and *trans*-1,2-dichlorodifluoroethylene[6] have molar refractions at 0° of 20.49 and 20.61. It is likely that 19.44 is correct for one of the two forms, since compound **69**, on which the value is based, was reported[22] to freeze sharply. However, even if this is so, it is not known to which of the isomers the value applies.

(82) There is some indication that Cl in *allylic* $CClF_2$, CCl_2F, and CCl_3 groups is not invariant. Thus, compounds **72**, **77**, **78**, and **79** yield successive increments for Cl − F of 4.99, 4.87, and 4.54. However, the data are too meager at present to warrant assigning separate values. This point should be re-examined as more data become available.

(83) f = 10, see ref. 47.

(84) Compound **97** is a cyclopentene containing the necessarily *cis*-$CCl{=}CCl$ group with a group refraction of 18.550. While this value includes an unknown ring exaltation, this is probably fairly small. It may therefore be significant to note that this value is very similar to the one derived for $CCl{=}CCl$ from the open chain olefins **85–87**.

TABLE IX

MOLAR REFRACTION OF PERHALO OLEFINS WITH INTERNAL DOUBLE BONDS[a]

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	R_{add} (Table XII)
85a	*b*	$CF_3CCl{=}CClCF_3$[c]		30.55_2	
85b	*d*	$CF_3CCl{=}CClCF_3$[c]		30.64_9	
85c		$CF_3CCl{=}CClCF_3$[c]	30.78	30.60_0 (av.)	30.7
86	*e*	$CBrF_2CCl{=}CClCBrF_2$[c]	46.03	46.05_8	46.0
87	*f*	$CF_3CCl{=}CClCF_2CF_3$	35.68	35.54[g]	35.6
88	*h*	$CCl_3CCl{=}CClCCl_3$[c]	59.14	58.78_2[i]	59.8[i]
89	*h*	$CClF_2CF{=}CClCF_3$[c]	30.78	30.60_7	30.4
90	*h*	$CCl_3CF{=}CClCF_3$[c]	40.23	39.86_3	40.2
91a	*d*	$CF_3CF{=}CClCF_3$		25.71_5[j]	
91b	*h*	$CF_3CF{=}CClCF_3$		25.85_1	
91c		$CF_3CF{=}CClCF_3$	26.05	25.78_3	25.6
92	*k*	$CBrF_2CF{=}CFCBrF_2$[c]	36.58	36.81_4	36.5
93	*h*	$CF_2ICF{=}CFCF_2CCl_3$[c]	53.06	53.18_6	53.0
94	*h*	$CBrF_2CF{=}CFCF_2CCl_3$	48.03	47.35_4	47.8
95	*k*	$CClF_2CF{=}CFCClF_2$	30.78	30.93_9	30.9
96	*l*	$CCl_3CF_2CF{=}CFCF_2CCl_3$	59.48	59.06_7[g]	59.1
97	*m*	$CF_2CCl{=}CClCF_2CF_2$[c]	33.20	33.29_2	*n*

[a] Includes all internally unsaturated perhalo olefins for which four place densities and refractive indices are available. All of these compounds except **97** can exist as *cis–trans* isomers. [b] Ref. 51. [c] Freezing points were reported on these samples. [d] Ref. 19. [e] Ref. 85. [f] Ref. 86. [g] Corrected to 20.0°; see text. [h] Ref. 63. [i] Very far out of line; may be a different isomer; omitted from the calculations. [j] Reported[19] 23.7; recalculation gave 25.71_5. [k] Ref. 87. [l] Ref. 88. [m] Ref. 89. [n] Employed to determine the group refractions for CCl=CCl in cyclopentenes.

TABLE X

MOLAR REFRACTION OF MISCELLANEOUS PURE PERHALO COMPOUNDS

No.	Ref.	Compd.	R_{exp}
98	*a*	CCl_4	26.44_8
99	*b*	$CBrCl_2F$	24.33_7
100	*c*	$CBrCl_3$	29.29_4
101	*d*	CBr_3F	30.05_9
102a	*b*	CCl_2FI	29.66
102b	*e*	CCl_2FI	29.56
102c		CCl_2FI	29.61 (av.)
103	*b*	CCl_3I	34.80_5
104	*f*	$CClF{=}CClF$ (*cis*)	20.54[g]
105	*f*	$CClF{=}CClF$ (*trans*)	20.66[g]
106	*h*	$CCl_2{=}CClF$	25.36_2
107	*a*	$CCl_2{=}CCl_2$	30.30
108	*i*	$CF_2{=}CClCCl{=}CF_2$	29.70_1
109	*i*	$CCl_2{=}CClCCl{=}CCl_2$	49.89_2
110	*b*	$CCl{=}CClCCl{=}CClCCl_2$	52.01_6
111	*j*	$CF_2CF_2CF_2CF_2CF_2$	24.50[g]
112	*k*	$CF_3CF_2CF_2CF(CF_3)_2$	26.81[g]

[a] Ref. 27. [b] Ref. 63. [c] Ref. 95. [d] Ref. 96. [e] Ref. 97. [f] Ref. 6. [g] Corrected to 20.0°; see text. [h] Ref. 64. [i] Ref. 58 and 59. [j] Ref. 40 and 98. [k] Ref. 41.

The Eisenlohr values fit the molar refractions found for the 13 compounds[19,51,63,85–89] of Table IX with a probable error[57a] of 0.20. The values herein provisionally proposed lead to no significant improvement for this set of compounds. The uncertainty concerning the possible differences in refraction for allylic chlorine[82] in CCl_3, CCl_2F, and $CClF_2$ does not appear to be large enough to account for more than a small fraction of the discrepancies. On the other hand, *cis–trans* isomerism can easily be responsible. Thus, there is some reason to believe that molar refraction may prove to be a powerful tool in helping to establish such configuration.

Perhalocyclobutenes.—Molar refractions for eight perhalocyclobutenes are listed in Table VII. The differences between compounds **59** and **60**, and between **61** and **63** yield values for Cl − F; they give 6.08 ± 0.02 for allylic chlorine in cyclobutenes. The difference between **64** and **65** is Br − F; this gives 8.87 for allylic bromine in cyclobutenes. The differences between **59** and **63** and between **61** and **62** yield values for I − F; these give 14.1 ± 0.15 for allylic iodine in cyclobutenes. These values, while slightly higher, are within experimental error of those already determined for terminal allylic halogen in open-chain structures. Thus, from a practical point of view, there does not appear to be justification for retaining two sets of values at present. For this reason, the atomic refractions determined for terminal allylic halogen in open-chain perhalo olefins were employed to calculate the group refraction for CF=CF in cyclobutenes, 8.80 ± 0.07.[90] Compound **66** gives for CCl=CCl in cyclobutenes 18.89. These group refractions of course include whatever contributions are made by the four-membered rings. It is not possible at present to separate these contributions, nor, from a practical point of view, is it necessary.

The Eisenlohr increments fit the molar refractions for the eight cyclobutenes listed in Table VII with a probable error[57a] in R_{add} of 0.14. The eight pieces of data were used to calculate two parameters; the probable error[57c] of the fit employing them is 0.06.

Other Group and Atomic Refractions in Perhalo Compounds.—Table X lists molar refractions for some pure perhalo compounds,[6,27,40,41,58,59,63,64,95–98] most of which are special cases. Thus, because the necessity for different values for chlorine and bromine in CX_2 and CX_3 has been demonstrated, it is not surprising that still another set of values should be required for these atomic refractions in CX_4. Thus, compound **98** gives 5.97 for chlorine; compounds **99–101** give 8.7_5 ± 0.04 for bromine; and compounds **103** and **104** give $14._1$ ± 0.2 for iodine.

The four perhaloethylenes listed in Table X (compounds **104–107**) constitute another special class, with which little can be done at present. The 1,2-dichlorodifluoroethylenes point up the effect on molar refraction of *cis–trans* isomerism.

Butadienes, compounds **108** and **109**, yield, on subtraction of the proper vinyl group refractions, exaltations of 0.62 and 0.97, respectively, for 1,3-conjugation.

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(85) F. W. McLafferty, Ph.D. Thesis, Cornell University, 1950.

(86) A. L. Henne and K. A. Latiff, *J. Am. Chem. Soc.*, **76**, 610 (1954).

(87) H. Kaldon, M.A. Thesis, Cornell University, 1952.

(88) A. L. Henne and D. W. Kraus, *J. Am. Chem. Soc.*, **76**, 1175 (1954).

(89) A. L. Henne and W. J. Zimmerschied, *ibid.*, **67**, 1235 (1945).

(90) Using the values for allylic halogen as determined from the cyclobutenes themselves, the value for CF=CF becomes 8.70 ± 0.06.

(91) R. G. Benner, *et al.*, *Ind. Eng. Chem.*, **39**, 329 (1947).

(92) Little or no evidence bearing on the purity of these compounds was available.

(93) E. T. McBee and L. D. Bechtol, *Ind. Eng. Chem.*, **39**, 380 (1947).

(94) E. T. McBee and W. B. Liggett, U. S. Patent 2,614,129 (Oct. 14, 1952); *Chem. Abstr.*, **47**, P8769*g* (1953).

(95) R. R. Dreisbach, "Physical Properties of Chemical Compounds," Vol. II, American Chemical Society, Washington, D. C., 1959, p. 199.

(96) Y. Desirant, *Bull. soc. chim. Belges*, **67**, 676 (1958); *Chem. Abstr.*; **53**, 17017*i* (1959).

(97) J. Fried and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 2078 (1959).

(98) G. H. Rohrback, *J. Chem. Phys.*, **17**, 547 (1949).

TABLE XI

AGREEMENT BETWEEN EXPERIMENTAL AND ADDITIVE MOLAR REFRACTIONS

Compd.	No. of compd., n	No. of parameters, f	Probable error[47] in R_{add}	Average fit, % of R_{exp}
Perhalo-*n*-alkanes				
containing Cl, F only	32	3	0.03	±0.09
containing Br, Cl, F	17	2	0.04	±0.13
Perhalocyclobutanes	4	3	<0.01	0
Perhalocyclobutenes	7	2	0.06	±0.2
Perhalo olefins				
terminally unsatd.	18	10	0.09	±0.2
internally unsatd.	14	4	0.16	±0.5

There is no reason to expect that such exaltations should be invariant with structure.

Decafluorocyclopentane (**111**) gives a C_5 ring increment of −0.07. Five perfluorinated cyclohexanes[53,54,91,92] give a tentative value for the C_6 ring increment of −0.17 ±0.02. Nine saturated polycyclic compounds[39,54,92–94] give a tentative value of −0.22 ± 0.05 per ring.

Perfluoro-2-methylpentane (**112**) gives a chain-branching increment for the 2-methyl group of −0.09.

A tentative value of 1.71 ± 0.07 for ether oxygen in the group CF_2OCF_2 was derived from four open-chain perfluoro ethers.[38,92,99,100] This value also appears to be applicable to cyclic ethers,[38,92,101] provided the ring increments derived above are also employed.[102]

A tentative value for tertiary nitrogen of 2.5 ± 0.3 was derived from nine tertiary perfluoroamines. See ref. 38, 92, and 103–105.

Comparison of Molar Refractions Found and Calculated.—In Table XI are listed the precision of the fits of R_{add} obtained for the sets of compounds employed to determine the atomic and group refractions summarized in Table XII. These also provide a measure of what can be expected from the proper application of these refraction increments to other compounds. Thus, 95% confidence limits[48b] can be obtained by multiplying the probable errors in Table XI by a factor of three. In general, the saturated perhalo compounds, except the iodides, can be expected to be fitted within ±0.1% of R_{exp}; perhalo olefins not capable of *cis–trans* isomerism, ±0.2%; and iodides and perhaloolefins capable of *cis–trans* isomerism, *ca.* ±0.5%. It is anticipated that as additional dependable data become available, these fits can be materially improved.

TABLE XII

SUMMARY OF ATOMIC AND GROUPS REFRACTIONS FOR PERHALO COMPOUNDS

Compounds or structures applicable to	Atom or group	R^{20}_{D}
All perhalo compounds	C	2.584[a]
	F	1.165[b]
Perhalo-*n*-alkanes[c]	Cl (in CX_4)	5.97[d]
	Cl (in CX_3)	5.850 ± 0.007
	Cl (in CX_2)	5.69 ± 0.02
	Br (in CX_4)	8.75 ± 0.04
	Br (in CX_3)	8.57 ± 0.05
	Br (in CX_2)	8.19 ± 0.03
	I (in CX_4)	14.1[d]
	I (in CX_3)	13.7[e]
	I (in CX_2)	12.7[d]
Perhalocyclobutanes	Cl	5.90[d]
	Br	8.59[d]
Ring increments (saturated)	C_4 ring	0.10[d]
	C_5 ring	−0.07[d]
	C_6 ring	−0.17 ± 0.02[f]
Polycyclic compounds (saturated)	Per ring	−0.22 ± 0.05[f]
Perfluoro ethers	O	1.71 ± 0.07[f]
Perfluoroamines (tertiary)	N (tertiary)	2.5 ± 0.3[f]
Perhalo olefins	$CF_2{=}CF$	10.15[d]
	$CF_2{=}CCl$	14.54[d]
	$CCl_2{=}C<$	18.49[d]
	$CCl_2{=}CF$	19.53[d]
	$CClF{=}CCl$	19.4[d,g]
	$CCl_2{=}CCl$	24.46 ± 0.03
	$CF{=}CF$	9.0[g]
	$CCl{=}CF$	13.4[g]
	$CCl{=}CCl$	18.5[g,h]
	Cl (in allylic CX_3)	6.03 ± 0.03[i]
	Cl (in open-chain allylic CX_2)	5.74[d]
	Br (in allylic CX_3)	8.82[d,i]
	I (in allylic CX_3)	14.0[d,e,i]
Perhalocyclobutenes	$CF{=}CF$	8.80 ± 0.07[j]
	$CCl{=}CCl$	18.9[d,j]

[a] Derived from *n*-alkanes; assumed for perhalo compounds. [b] Derived from perfluoropentane and perfluoroheptane; assumed for fluorine bonded to carbon in all perhalo compounds. [c] Values listed under this entry are also assumed applicable to saturated nonallylic portions of perhalo olefins, *e.g.*, to Cl in $CF_2{=}CFCF_2CCl_3$. [d] Based on only one or two compounds; considered tentative. [e] May vary widely with structure; see text. [f] Based on compounds the purity of which was not demonstrated. [g] These values are very uncertain, apparently because these groups can exist as *cis–trans* isomers; see text. [h] Also applicable to cyclopentenes. [i] Also applicable to allylic halogen in cyclobutenes. [j] Includes ring increment.

In Table XIII are listed molar refractions for three groups of perhalo compounds not previously considered in this paper. These compounds were not employed in the refractivity calculations because of lack of sufficient evidence demonstrating their purity. Compounds **113–140**[6,15,19,37–39,55,60,63,70,74,96,106–118] are saturated perhalocarbons containing only fluorine, chlorine, and bromine; compounds **141–150**[56,63,74,96,113,116,119,120] also contain iodine; and compounds **151–165**[19,70,97,116,121–126] are terminally unsaturated olefins.

In the first group, compounds **113–131** are fitted by the atomic refractions of Table XII with a probable error[57a] in R_{add} of 0.037. Agreement of this order clearly constitutes strong supporting evidence for the structure and purity of these compounds.

Of the saturated iodides, compounds **141–146** are fitted by R_{add} with a probable error of 0.11; of the olefins, compounds **151–159** are fitted with a probable error of 0.09.

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(99) A. L. Henne and M. A. Smook, *J. Am. Chem. Soc.*, **72**, 4378 (1950).

(100) J. H. Simons, U. S. Patent 2,500,388 (Mar. 14, 1950); *Chem. Abstr.*, **44**, P5236*d* (1950).

(101) E. A. Kauck and J. H. Simons, U. S. Patent 2,644,823 (July 7, 1953); *Chem. Abstr.*, **48**, P6469*i* (1954).

(102) For determining ring size, oxygen is regarded as equivalent to carbon; *e.g.*, *c*-$C_5H_{10}O$ requires a C_6 ring increment.

(103) R. N. Haszeldine, *J. Chem. Soc.*, 102 (1951).

(104) E. A. Kauck and J. H. Simons, British Patent 666,733 (Feb. 20, 1952); *Chem. Abstr.*, **46**, P6015*g* (1952).

(105) E. A. Kauck and J. H. Simons, U. S. Patent 2,616,927 (Nov. 4 1952); *Chem. Abstr.*, **47**, P8772*b* (1953).

TABLE XIII

MOLAR REFRACTIONS OF PERHALO COMPOUNDS FOR WHICH SUFFICIENT EVIDENCE FOR PURITY IS LACKING

No.	Ref.	Compd.	R_{add} (Eisenlohr)	R_{exp}	R_{add} (Table XII)
113a	*a*	CCl_3F		21.66^b	
113b	*c*	CCl_3F		21.61	
113c		CCl_3F	21.56	21.63_5 (av.)	21.66
114	*d*	$CClF_2CClF_2$	21.73	21.52^b	21.53
115	*e*	$CCl_3CClFCClF_2$	40.81	40.34	40.34
116	*f*	$CBrF_2CF_2CBrF_2$	32.42	31.87	31.88
117	*g*	$CCl_3CF_2CBrFCF_3$	43.88	43.14	43.07
118	*h*	$CBrF_2CBrFCF_2CF_3$	37.32	36.47^b	36.42
119	*h*	$CBrF_2CF_2CF_2CBrF_2$	37.32	36.84^b	36.80
120	*i*	$CCl_3CF_2CF_2CF_3$	36.25	36.05^b	36.04
121	*j*	$CF_3CCl_2CClFCF_3$	36.25	35.59^b	35.56
122	*k*	$CClF_2CCl_2CF_2CClF_2$	40.98	40.46	40.41
123	*g*	$CClF_2CClFCCl_2CF_3$	40.98	40.26	40.26
124	*g*	$CCl_3CClFCCl_2CF_3$	50.43	49.67	49.63
125	*l*	$CCl_2FCClFCClFCCl_2F$	50.43	49.79	49.78
126	*m*	$CCl_3CCl_2CF_2CCl_3$	59.89	59.16	59.15
127	*n*	$n\text{-}C_5F_{11}Br$	34.59	34.29^o	34.30_5
128	*p*	$CF_3CCl_2CCl_2CF_2CF_3$	45.88	44.87	45.00
129	*q*	$(CClF_2CClFCClF)_2$	60.23	59.23^b	59.28
130	*q*	$(CCl_2FCClFCClF)_2$	69.68	68.76^b	68.62
131	*r*	$CBrF_2CBrFCF_2CF_2CClFCClF_2$	56.57	55.41	55.45
132	*s*	$(CClF_2CClFCF_2CF_2)_2$	60.57	60.57	60.06
133	*t*	$CClF_2CF_2CF_3$	21.90	21.93^b	21.76
134	*u*	$CCl_3CF_2CF_3$	31.36	31.24^b	31.13
135	*h*	$CF_3CBrFCBrFCF_3$	37.32	34.46^b	36.04
136	*n*	$n\text{-}C_5F_{11}Cl$	31.70	31.74	31.58_5
137a	*v*	$n\text{-}C_6F_{14}$	31.87	31.69^b	31.81
137b	*w*			32.02^b	
138a	*w*	$n\text{-}C_8F_{18}$	41.66	41.97^b	41.64
138b	*x*			42.12	
139a	*y*	$n\text{-}C_9F_{20}$	46.56	46.76^b	46.56
139b	*x*			47.01	
140	*z*	CBr_2F_2	22.63	22.12^b	22.4_1
141	*aa*	$CClF_2CClFI$	34.39	34.01^b	$34._1$
142	*r*	$CClF_2CClFCF_2CClFI$	48.91	48.36	$48._4$
143	*r*	$CClF_2CCl_2CF_2CClFI$	53.64	53.13	$53._0$
144	*s*	$CClF_2CClFCF_2CF_2CF_2CF_2I$	53.98	53.45	$53._6$
145	*n*	$n\text{-}C_5F_{11}I$	39.63	39.24	$39._4$
146	*aa*	CCl_2FCF_2I	34.39	33.85	$34._1$
147	*g*	$CClFICF_2CF_3$	34.56	34.77	$34._3$
148	*g*	$CF_3CFICF_2CF_3$	34.73	33.88	$33._5$
149	*bb*	CF_2ICF_3	24.94	23.81^b	$24._7$
150	*cc*	CF_2ICF_2I	37.60	38.85^b	$37._3$
151	*dd*	$CF_2{=}CFCCl_2F$	25.88	25.97	25.9_6
152	*ee*	$CF_2{=}CFCF_2CCl_2F$	30.78	30.47	30.5_1
153	*s*	$(CF_2{=}CFCF_2CF_2CF_2CF_2)_2$	59.76	59.58	59.6_1
154	*ff*	$\overline{CF{=}CFCBrFC}ClF$	31.20	31.17	30.1_2
155	*ff*	$\overline{CF{=}CF{-}CBrFC}FI$	39.13	38.99	$39._1$
156	*s*	$(CF_2{=}CFCF_2CF_2)_2$	40.17	40.19	39.9_6
157	*s*	$(CF_2{=}CFCF_2CF_2CF_2)_2$	49.97	49.58	49.7_8
158	*gg*	$CF_2{=}CFCClFCClF_2$	30.78	30.55^b	30.3_8
159	*hh*	$CF_2{=}CF(CF_2)_4I$	43.78	43.45	$43._5$
160a	*ii*	$CCl_2{=}CFCClF_2$	30.61	30.31^b	30.4_7
160b	*ii*			30.70^b	
161	*k*	$CCl_2{=}CClCF_2CF_3$	35.51	35.01	35.4_5
162	*jj*	$CCl_2{=}CFCCl_2F$	35.34	37.62	35.3_4
163	*hh*	$CF_2{=}CF(CF_2)_6I$	53.58	54.84	$53._3$
164	*kk*	$CF_2{=}CFClF_2CCl_2I$	43.44	42.10	$43._0$
165	*kk*	$CF_2{=}CFCF_2CFI_2$	46.64	46.80	$46._2$

[a] Ref. 106 and 107. [b] Corrected to 20.0°, see text. [c] Ref. 108. [d] Ref. 6. [e] Ref. 109. [f] Ref. 15. [g] Ref. 63. [h] Ref. 110. [i] Ref. 111. [j] Ref. 112. [k] Ref. 19. [l] Ref. 69. [m] Ref. 60. [n] Ref. 113. [o] Interpolated between data at 0 and at 28°. [p] Ref. 114. [q] Ref. 115. [r] Ref. 74. [s] Ref. 116. [t] Ref. 117. [u] Ref. 118. [v] Ref. 37. [w] Ref. 38. [x] Ref. 55. [y] Ref. 39. [z] Ref. 96. [aa] Ref. 119. [bb] Ref. 56. [cc] Ref. 120. [dd] Ref. 97. [ee] Ref. 121. [ff] Ref. 70. [gg] Ref. 122. [hh] Ref. 123. [ii] Ref. 124. [jj] Ref. 125. [kk] Ref. 126.

In view of the present uncertainties in the refractive increments for iodine and for unsaturated groups, no conclusion will be drawn about the poor fits for compounds **147–150** and **160–165**. However, the remaining nine compounds, **132–140**, fall well outside of the 95% confidence limits. It is therefore concluded that the densities and/or refractive indices reported for these compounds must be seriously in error.

In this connection, it is of interest to note that an error of 0.0004 in $n^{20}\mathrm{D}$ produces an error of *ca.* 0.1% in R_{add}. For the density term, a given per cent error in density will cause the same per cent error in R_{add}. Since in many cases a change in refractive index arising from the presence of impurity will be partially compensated for by a change in density, a poor refractivity check must be taken as evidence for really gross error in refractive index and/or density.

The present work demonstrates that under the proper circumstances molar refractivity can be a considerably sharper tool than has heretofore been commonly realized. Thus, in the perhalo compounds, it can serve not only as supporting evidence for molecular formula, but also to distinguish between certain types of position isomers. Furthermore, it can be used, particularly for the alkanes, as a necessary, although not sufficient, criterion of purity. Its greatest value in this connection may be for spotlighting inaccurate densities and/or refractive indices. A possible application to determination of the configuration of *cis–trans* isomers has already been pointed out.

Compounds Containing Halogen and Hydrogen.—Further studies aimed at setting up a system of refraction increments for hydrogen-containing halogen compounds are under way. The consideration of such compounds is inherently much more complex than has been found to be the case with the perhalo compounds, apparently because of the greatly increased effect of interactions of nonbonded atoms. Remick[127] has pointed out that the changing values of the successive differences in molar refraction in the series CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, CH_4 indicates that the refractions of both hydrogen and chlorine are altered by substitution, "as it is quite inconceivable that only one of

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TABLE XIV

REFRACTION VARIATIONS WITH SUBSTITUTION OF H BY F

Structure	Group refraction	ΔR	R_F[b]
CH_2CH_3	10.31		
		−0.12	
CH_2CH_2F	10.19[a]		0.906
		0.04	
CH_2CHF_2	10.23[c]		0.988
		0.16	
CH_2CF_3	10.39[c]		1.055

[a] Based on the data of Jeffery, *et al.*,[129] on *n*-alkyl fluorides.
[b] Assuming C and H constant at 2.584 and 1.029, respectively.
[c] Ref. 50.

them would be altered." The same effect is demonstrated for hydrogen and fluorine in Table XIV, to which Remick's statement is equally pertinent.

For the present, in order to treat highly halogenated compounds containing one or two hydrogen atoms, a tentative value of 1.0 is suggested for R_H.

Experimental

Determination of Physical Properties.[128] **Measurement of Temperature.**—One to five junction calibrated copper-constantan thermocouples were used to measure temperature. E.m.f. was measured with a Rubicon potentiometer Model 2733, or with a Brown "Electronik" continuous balance recording potentiometer, full scale reading 5 mv., with range extended by a stable bucking circuit.

Fractional Distillation and Boiling Point.—Compounds boiling above room temperature were fractionally distilled through a glass helix packed column, 52 × 1.5 cm., with an electrically heated jacket, and a variable takeoff head fitted with a five-junction thermocouple. The latter was calibrated *in situ* by fractional distillation of the set of standard liquids recommended for this purpose by Timmermans.[130]

For compounds boiling below room temperature, a vacuum-jacketed column identical with the above was employed, but with a Dry Ice cooled variable takeoff head fitted with a one-junction bare wire thermocouple.

All liquids were treated with P_2O_5 prior to distillation. For those boiling higher than *ca.* 75°, the P_2O_5 was filtered off, while for lower boiling compounds, the materials were fractionally distilled from the P_2O_5.

Observed boiling points t_0 at pressure[131] p_0 (mm.) given in this section are considered accurate to ±0.1° for the range 25 to 115°, and to ±0.2° for the range −30 to +25°, and 115 to 200°. Boiling points listed in Tables I and II were corrected to 760 mm. using the equation $t_C = t_0 + 0.043\,(760 - p_0)$.[132] For the compounds involved over the range 720–760 mm., this correction was found to be reproducible to within ±0.1°. The boiling range listed in Tables I and II is that of the center cut on which all other physical properties were taken.

Cooling Curves and Freezing Points.—For all compounds which could be crystallized, cooling curves were run as a criterion of purity. The apparatus consisted of a flat-bottomed tube with an evacuatable jacket, fitted with a motor-driven reciprocating cage stirrer. The tendency of some compounds to form a solid plug on the bottom rather than a slush, thereby hindering the attainment and maintenance of equilibrium, was substantially eliminated by use of a highly evacuated false bottom. This was found to cut down on heat flow through the bottom and to favor crystallization taking place on the side walls of the tube, where the cage stirrer was most effective. Temperature was measured with a multiple junction thermocouple, the bare wires and junctions of which were supported in the liquid on a strip of Kel-F plastic. In most cases, the sample size was 20 ml., for which a five-junction thermel was used. Where only 2–4 ml. of material was available, a smaller apparatus, using a two-junction thermel, was employed. Both thermels were calibrated *in situ* by running cooling curves on the series of carefully purified liquids recommended by Skau[133] for this purpose. All freezing points reported to a tenth of a degree are considered accurate to better than ±0.2°.

Freezing points listed in Tables I and II are the maximum equilibrium temperatures found. For most compounds, this was the initial temperature reached just after supercooling ended; for some, it was the highest temperature reached in a sluggish return to equilibrium: and for a few, it was the equilibrium temperature at which the last crystals melted, in a warming curve. The freezing point depressions listed in Table I and II were taken from each cooling curve at the point at which it was estimated that 50% of the material had frozen. Inasmuch as the molal freezing point depressions for perhalo compounds are very large (*e.g.*,[134] for CCl_2FCCl_2F and CCl_3CClF_2, *ca.* 38°/1000 g.-mole), freezing point depressions of 0.2° or less are evidence for very high purity with respect to compounds capable of depressing the freezing point.

Density and Refractive Index.—Relative densities[135] $d^{20}{}_4$ were taken at 20.00 ± 0.05° on samples of 10 or 25 ml., using pycnometers described by Bauer, *et al.* (p. 149,[135] type D), the samples being distilled directly into the pycnometer. Calibrated weights were employed, and corrections were applied for the bouyant effect of air, and, for liquids boiling below 50° for the weight of vapor in the free space above the liquid.[135] The pycnometers were calibrated with freshly boiled distilled water, and checked with purified benzene (found, $d^{20}{}_4$ 0.87894; reported[27] 0.87888–0.87909) and methanol (found $d^{20}{}_4$ 0.79140; reported[27] 0.7913–0.7915). The densities are considered accurate to ±0.0002 g./ml.

Refractive indices for the sodium D-line were taken with a standard Abbe refractometer, equipped with a calibrated thermometer accurate to ±0.1°. The refractometer was checked with a set of pure liquids over the range 1.33 to 1.55; for these, the literature values were consistently reproduced within ±0.0001 unit.

Molecular Weights.—For compounds boiling below 40–60°, molecular weights accurate to ±2% were determined by vapor density. For higher boiling compounds, depression of the freezing point of benzene gave results of similar accuracy.

1,1,2-Trichlorotrifluoroethane.—Photochemical chlorination of $CClF{=}CF_2$, b.p. −29.0° (734 mm.), gave CCl_2FCClF_2 (I), b.p. 46.3° (728 mm.), plus telomers[136] (dimer, trimer, and higher polymers). Further work on structure of the telomers is in progress.

1,1,1-Trichlorotrifluoroethane.—This compound, available from earlier work,[137] was fractionally distilled to give a center cut II, b.p. 44.9° (724 mm.).

2,2-Dichloropropane.—Isopropyl chloride, b.p. 34–35°, was chlorinated photochemically[138] at 12–22° to give 50–60% recovered $CH_3CHClCH_3$; 48–53 mole % $CH_3CCl_2CH_3$, center cut III, b.p. 68.8° (743 mm.); 31–34 mole % $CH_2ClCHClCH_3$, center cut IV, b.p. 95.8° (743 mm.); and 1.5–3 mole % of trichloride. This method is superior from a large-scale preparative standpoint to the more usual one involving treatment of acetone with PCl_5.[13,139]

1,1,1,3,3,3-Hexachlorodifluoropropane.—The reaction sequence $CH_3CCl_2CH_3 \rightarrow CH_3CF_2CH_3 \rightarrow CCl_3CF_2CCl_3$ was employed. The fluorination of 8.5 moles of $CH_3CCl_2CH_3$ with a 25% excess of SbF_3 and 5 wt.% of Br_2 gave 6.3 moles of $CH_3CF_2CH_3$, b.p. −0.8 to +1.0° (74% conversion); 0.7 mole of $CH_3CClFCH_3$, b.p. 34–35° (8% conversion), center cut V, b.p. 34.5–34.9° (738 mm.); and 0.2 mole of recovered $CH_3CCl_2CH_3$ (2% of starting material). The temperature required for reasonable rate of reaction, 55°, was much higher than that of Henne and Renoll,[13] who reported that the reaction was self-sustaining at room temperature.

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(128) See ref. 62 for a detailed discussion.

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Photochemical chlorination of the $CH_3CF_2CH_3$, using a 400-w. Westinghouse DH-1 mercury vapor lamp for illumination, gave $CCl_3CF_2CCl_3$ (VI), center cut b.p. 195.4° (743 mm.), in almost quantitative yield. Best results were obtained by holding the reaction mixture at very near reflux temperature throughout the reaction. It was found convenient to employ a Dry Ice cooled reflux condenser throughout the reaction; the condensed chlorine proved quite effective in washing back high melting intermediate chlorination products which otherwise tended to plug up the condenser.

In addition to $CCl_3CF_2CCl_3$, small amounts of higher boiling material, b.p. 90–160° (20 mm.) and higher, were isolated. These appear to be dimeric products due to radical combination, and are under further investigation.

Fluorination of 1,1,1,3,3,3-Hexachlorodifluoropropane.—Fluorination of the $CCl_3CF_2CCl_3$ was carried out by the method of Henne and Flanagan,[17] using HgO and HF as the fluorinating agent. The reaction vessels were 400-ml. lecture cylinders fitted with steel valves, which were heated and agitated in a rocker-type shaker. One mole of $CCl_3CF_2CCl_3$, 0.5 mole of HgO, plus 6 moles of HF heated at 100° for 11 hr. gave 33 mole % recovered starting material; 35 mole % A, b.p. 155°; and 13 mole % B, b.p. 115°. At 165°, 0.5 mole of $CCl_3CF_2CCl_3$, 2.0 moles of HgO, and 14 moles of HF gave, in 12 hr., 45 mole % B; 28 mole % C, b.p. 75°; and 1 mole % D, b.p. 36°. At 190°, 0.5 mole of $CCl_3CF_2CCl_3$, 2.5 moles of HgO, and 13 moles of HF gave, in 26 hr., 16 mole % C and 59 mole % D.

Fractions A, B, C, and D, with successive 40° decreases in boiling point from that of the starting material, clearly involved successive substitutions of chlorine by fluorine. Thus A was a $C_3Cl_5F_3$, B was a $C_3Cl_4F_4$, C was a $C_3Cl_3F_5$, and D was a $C_3Cl_2F_6$. These molecular formulae were supported by the molecular weights given below. Thus, the only discussion required relates to position of the chlorine atoms undergoing substitution.

Since the starting material was the 2,2-difluoride, fraction A, center cut b.p. 154.5° (739 mm.), can only be $CCl_2CF_2CCl_2F$ (VII).

Anal. Calcd.: mol. wt., 270.5. Found: mol. wt., 268.5.

Henne, *et al.*,[11,13] reported physical properties for this compound (see Table I, density differs appreciably), but gave no method of preparation or evidence for structure. Coffman, Cramer, and Rigby[12] claimed to have prepared it from $CF_2{=}CClF$, CCl_4, and $AlCl_3$, but this has been disputed by Henne and Kraus,[140] who showed that the product of the aluminum chloride catalyzed reaction is principally $CCl_3CClFCClF_2$ contaminated by rearrangement products.

Fraction B, center cut b.p. 113.9° (740 mm.), was shown to be $CCl_2FCF_2CCl_2F$ (VIII). Thus, its molecular formula, indicated by boiling point to be $C_3Cl_4F_4$, is supported by its molecular weight.

Anal. Calcd.: mol. wt., 254. Found: mol. wt., 249.

The only other possibility, $CCl_3CF_2CClF_2$, is known[17]; its physical properties differ significantly from those of B; see Table I, compounds VIII and IX.

Young and Murray[14] reported the fluorination of $CCl_2FCF_2CCl_2F$ to yield $CClF_2CF_2CClF_2$; however, they gave no preparation for the tetrachloride, nor did they list its physical properties. Coffman, Cramer, and Rigby's[12] report of its preparation *via* the $AlCl_3$-catalyzed addition of CCl_3F to $CClF{=}CF_2$ is questionable.[140]

Fraction C, center cut b.p. 741.1° (739 mm.), indicated by boiling point to be a $C_3Cl_3F_5$, can only be $CCl_2FCF_2CClF_2$ (IX) since it was obtained by fluorination of VIII.

Anal. Calcd.: mol. wt., 237.5. Found: mol. wt., 240.

This compound has been reported by Coffman, Cramer, and Rigby[12] from the $AlCl_3$-catalyzed addition of CCl_3F to $CF_2{=}CF_2$; their product appears to have been very impure, since its refractive index differs markedly from that found for IX, after correcting for the difference in temperature; see Table I. Baker and Whaley[16] reported the preparation of $CCl_2FCF_2CCl_2F$ by the fluorination of $CCl_3CF_2CCl_3$ with SbF_3 and Cl_2, but gave no physical properties.

Fraction D, center cut b.p. 35.3° (741 mm.), indicated by boiling point to be a $C_3Cl_2F_6$, was identified as $CClF_2CF_2CClF_2$ (X).

Anal. Calcd.: mol. wt., 221. Found: mol. wt., 224.

The only other possible structure, $CCl_2FCF_2CF_3$, was ruled out on the basis that this would involve the preferential fluorination of a $-CClF_2$ group over a $-CCl_2F$ group. Furthermore, if the 1,1-dichloride had been formed, its further fluorination to $CF_3CF_2CF_2Cl$ would have been expected to occur under the reaction conditions, whereas no trace of product boiling lower than 35° was ever observed.

$CClF_2CF_2CClF_2$ has been prepared by chlorination of $CHF_2CF_2CHF_2$,[14] fluorination of $CCl_2FCF_2CCl_2F$,[14] treatment of the silver salt of perfluoroglutaric acid with Cl_2,[15] and fluorination of $CCl_3CF_2CCl_3$ with SbF_3 and Cl_2[16]; see Table I for comparison of physical properties.

1,1,1,3-Tetrachlorotetrafluoropropane.—This compound, available from earlier work, was fractionally distilled to give a center cut XI, b.p. 112.9° (738 mm.).

1,1,1,2,3,3,3-Heptachlorofluoropropane.—The sequences of reaction of Henne and Haeckl[18] was utilized. In the first step,

$$CH_2{=}CClCH_2Cl \xrightarrow{HF} CH_3CClFCH_2Cl \xrightarrow{Cl_2} CCl_3CClFCCl_3$$

these authors reported that heating 2 moles of HF with 1 mole of $CH_2{=}CClCH_2Cl$ for 8 hr. at 50–60° gave a 74% conversion to $CH_3CClFCH_2Cl$, 4% $CH_3CF_2CH_2Cl$, and 10% recovered olefin. To avoid the necessity of separating the addition product from unchanged olefin (these compounds boil only 4° apart), the proportion of HF to olefin was doubled, and the reaction time was increased to 12 hr. Under these conditions, $CH_2{=}CClCH_2Cl$, center cut XII, b.p. 92.8° (738 mm.), gave 17–26 mole % of $CH_3CF_2CH_2Cl$, center cut XIII, b.p. 55.1° (742 mm.); 38–41 mole % of $CH_3CClFCH_2Cl$, center cut XIV, b.p. 87.7° (739 mm.); 4–7 wt.% of an unidentified compound, b.p. 116.9–117.5° (741 mm.), $n^{20}{}_D$ 1.4506, $d^{20}{}_4$ 1.2616, containing chlorine but no fluorine; 7–12 mole % of $CH_2ClCCl_2CH_3$, center cut XV, b.p. 122.0° (745 mm.); and *ca.* 2% of a higher boiling residue.

Photochemical chlorination of $CH_2ClCClFCH_3$ was carried out in a cylindrical Pyrex flask heated by a spiral winding of nichrome ribbon. Illumination was provided by eight 15-w. ultraviolet fluorescent lamps[141] arranged vertically around the cylindrical reaction flask, and mounted inside a stainless steel cylinder, *ca.* 28-cm. diameter, which served both as a support and a reflector.[62] In the early stages of chlorination, the reaction mixture was held near reflux temperature. However, when the boiling point of the reaction mixture rose to *ca.* 180°, the rate of reaction fell off markedly. At this point, it was found that the rate was sharply increased by dropping the temperature to 100°, presumably because of the greatly increased concentration of chlorine in solution. Under these conditions, which contrast strongly with those found optimum for the perchlorination of $CH_3CF_2CH_3$, a substantially quantitative conversion to $CCl_3CClFCCl_3$, center cut XVIa, b.p. 140.8° (50 mm.), was obtained. From other runs which were not carried to completion, the following intermediates were isolated: $CHCl_2CClFCH_3$ (XVII), b.p. 115.9° (736 mm.); $CCl_3CClFCH_3$ (XVIII), b.p. 138.7° (736 mm.); $CHCl_2CClFCH_2Cl$ (XIX), b.p. 159.9° (736 mm.); and $CCl_3CClFCH_2Cl$ (XX), b.p. 101.5° (50 mm.).

Chlorination of $CH_3CClFCH_3$.—Henne and Renoll[13] reported that chlorination of $CH_3CClFCH_3$ gave a "splitting of the molecule" to yield CCl_3CCl_2F. In view of the ready chlorination of $CH_2ClCClFCH_3$ with no evidence of cleavage, it was of interest to check this report. The photochemical chlorination of $CH_3CClFCH_3$ (V, 118 g., 1.22 moles) under the conditions described above for the perchlorination of $CH_2ClCClFCH_3$, with reaction temperature of 100–170° in later stages, gave a substantially quantitative yield of $CCl_3CClFCCl_3$ (XVIb); there was no evidence of cleavage. It is possible that Henne and Renoll's[13] cleavage product "CCl_3CCl_2F, easily identified by its melting point," was really the intermediate chlorination product $CCl_3CClFCH_3$. The physical properties reported[6] for CCl_3CCl_2F, b.p. 137.9° (760 mm.), f.p. 101.3°, are very close to those found for $CCl_3CClFCH_3$; see compound XVIII, Table II.

Fluorination of 1,1,1,2,3,3,3-Heptachlorofluoropropane.—In a typical run, 0.5 mole of $CCl_3CClFCCl_3$ was treated with 1.3 moles of HgO and 6 moles of HF for 7–14 hr. at 100–110°; the temperature was then raised to 170° for 12–19 hr. The com-

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(140) A. L. Henne and D. W. Kraus, *J. Am. Chem. Soc.*, **73**, 5303 (1951).

(141) These fluorescent lamps (General Electric 360 BL), 2.5-cm. diameter, 45 cm. long, are an ideal source of cool, high intensity long-wave ultraviolet light, uncontaminated by short wave radiation. They are reported[142] to have the following spectral distribution: output in watts below 2800 Å., 0; 2800–3200 Å., ...; 3200–3800 Å., 1.2; 3800–5000 Å., 0.64; and >5000 Å., 0.09.

(142) "Mercury Lamps," Bulletin LS-103, General Electric Co., Cleveland, Ohio, Aug. 1947.

bined products of three runs gave 12 mole % of E, b.p. 151–153°; 39 mole % of F, b.p. 112–114°; and 16 mole % of G, b.p. 73–47; no lower boiling products were found. On the basis of boiling points, it was clear that E was a $C_3Cl_5F_3$, F was a $C_3Cl_4F_4$, and G was a $C_3Cl_3F_5$.

Fraction E, center cut XXI, b.p. 153.7° (744 mm.), was assigned the structure $CCl_2FCClFCCl_2F$ on the basis that the only alternate structures, (a) $CCl_3CClFCClF_2$ and (b) $CCl_3CF_2CCl_2F$, would involve the fluorination of $-CCl_2F$ or $-CClF-$groups in preference to a $-CCl_3$ group.

Henne and Newby[19] reported physical properties for $CCl_2FCClFCCl_2F$ (see Table I), but made no explicit statement about how or from what it was prepared.

Fraction F, center cut XXII, b.p. 113.3° (748 mm.), was assigned the structure $CCl_2FCClFCClF_2$ on the basis that the only alternative structures, (a) $CF_3CClFCCl_3$,[25] (b) $CCl_2FCF_2CCl_2F$ (VIII), and (c) $CClF_2CF_2CCl_3$ (XI), would involve the fluorination of $-CClF_2$ or $-CClF-$ groups in preference to a $-CCl_2F$ or $-CCl_3$ group. Furthermore, the three alternate compounds are known; their physical properties, particularly density, are markedly different from those of XXII.

Repeated attempts to crystallize XXII were unsuccessful. It remained fluid for a number of hours at −120 to −140° with continuous stirring. It was completely fluid to −120°; below this point its viscosity increased rapidly until at −150° it was a hard glass. The material was a pure compound, however, as indicated from the high purity of its precursor XXI and of its fluorination product XXIII.

The physical properties found for XXII differ markedly from those previously reported[25] for $CCl_2FCClFCClF_2$, the identification of which is questioned.[62]

Fraction G, center cut XXIII, b.p. 73.0° (741 mm.), was assigned the structure $CClF_2CClFCClF_2$ on the basis that the only alternative formulations, (a) $CCl_2FCClFCF_3$,[20] (b) $CCl_2FCF_2CClF_2$ (IX), and (c) $CCl_3CF_2CF_3$,[118] would have involved the fluorination of $-CF_2Cl$ or $-CClF-$ groups in preference to $-CCl_2F$ or $-CCl_3$ groups. Furthermore, the three alternate compounds are known; their physical properties differ markedly from those of XXIII. Finally, its properties are substantially identical with those reported for $CClF_2CClFCClF_2$ from fluorination of $CCl_3CClFCClF_2$[20], and from reaction of chlorine with $CF_2{=}CFCBrF_2$[21] and $CHF_2CClFCClF_2$.[21]

1,2-Dichlorohexafluoropropane.—This compound, prepared by the addition of chlorine to $CF_2{=}CFCF_3$, was fractionally distilled to give a center cut XXIV, b.p. 33.7° (734 mm.).

1,1,1,2,3,3-Hexachlorodifluoropropane.—Gavlin[143] prepared $CCl_3CClFCCl_2F$ (XXV) by addition of F_2 to $CCl_3CCl{=}CCl_2$; his preparation was characterized; see Table I.

2-Chloroheptafluoropropane.—A sample of $CF_3CClFCF_3$, prepared[144] by adding F_2 to $CF_2{=}CClCF_3$, was fractionally distilled to give a center cut XXVI, b.p. −3.0° (742 mm.)

1,1,1,2,2-Pentachlorotrifluoropropane and 1,2,2-Trichloropentafluoropropane.—Photochemical addition of chlorine, using two long-wave ultraviolet lamps[141] for illumination, to $CCl_2{=}CClCF_3$, b.p. 87.2–87.4° (736 mm.), at 70–140° gave a substantially quantitative yield of $CCl_3CCl_2CF_3$, center cut XXVII, b.p. 152.1° (739 mm.). Fluorination of 0.36 mole of XXVII with 0.55 mole of HgO and 7 moles of HF by heating at 90–140° for 3 hr., at 150° for 12 hr., then at 160–180° for 3 hr., gave a 65% yield of $CClF_2CCl_2CF_3$, center cut XXVIII, b.p. 71.1° (737 mm.); nothing boiling lower was found.

1,1,1,2,2,3-Hexachlorodifluoropropane and Its Fluorination Products.—Photochemical addition of chlorine at 25–40° to $CCl_2{=}CClCClF_2$, b.p. 67.5° (100 mm.), f.p. −103.8°, using the apparatus described above for chlorination of $CH_2ClCClFCH_3$, gave a substantially quantitative yield of $CCl_3CCl_2CClF_2$, center cut XXIX, b.p. 193.8° (741 mm.). This compound has previously been prepared by chlorination of $CHCl_2CCl_2CClF_2$[11] and $CHF_2CH_2CH_3$.[23]

Fluorination of $CCl_3CCl_2CClF_2$ was carried out by a modification of the procedure of Henne and Ladd.[11] A mixture of 287 g. of $CCl_3CCl_2CClF_2$ (1.00 mole), 179 g. of SbF_3 (1.00 mole), and 30 g. of $SbCl_5$ (0.10 mole) was heated in a lecture cylinder to 155–165° for 12 hr. with shaking. The reaction product was poured on cracked ice, steam distilled, dried over P_2O_5, and fractionally distilled to give $CClF_2CCl_2CClF_2$, center cut XXX, b.p. 111.4° (740 mm.), in almost quantitative yield. A small amount of the intermediate $CCl_2FCCl_2ClF_2$, center cut XXXI, b.p. 151.8° (727 mm.), was also produced.

The fluorination of $CCl_3CCl_2CClF_2$ to give $CCl_2FCCl_2CClF_2$ and $CClF_2CCl_2CClF_2$ has previously been reported.[24] The structural formula $CClF_2CCl_2CClF_2$ there postulated for the tetrafluoride as a "plausible hypothesis" has been substantiated, for the compounds corresponding to the only alternative formulations, $CCl_2FCClFCClF_2$ (XXII) and $CCl_2FCCl_2CF_3$,[145] have since been synthesized; their physical properties turn out to differ substantially from those of $CClF_2CCl_2CClF_2$.

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