129. *Organic Fluorides. Part VI. The Chemical and Physical Properties of Certain Fluorocarbons.*

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The boiling points, densities, refractive indices, and surface tensions of a number of fluorocarbons have been determined, and the variation of certain of these properties with temperature has been investigated.

IN Parts I—V of this series (*J.*, 1949, 3021, 3026; 1950, 2689, 2787, 3617) the preparation of fluorocarbons by the interaction of fluorine and of cobalt trifluoride with hydrocarbons was described. The present communication records physical properties of certain fluorocarbons the preparation of which was described in Parts III—V.

The pure fluorocarbons available were: in the *n*-perfluoroparaffin series, C_7F_{16}, C_8F_{18}, C_9F_{20}, $C_{10}F_{22}$, $C_{11}F_{24}$, $C_{12}F_{26}$, and $C_{16}F_{34}$; the following monocyclic compounds, C_7F_{14}, C_8F_{16} (from *m*-xylene), C_9F_{18} (from mesitylene), and $C_{10}F_{20}$ (from *p*-cymene); and two bicyclic compounds, $C_{10}F_{18}$ (from naphthalene) and $C_{11}F_{20}$ (from 2-methylnaphthalene). The physical properties of some of these compounds have been described by Grosse and Cady (*Ind. Eng. Chem.*, 1947, **39**, 367) and by Fowler *et al.* (*ibid.*, p. 375), and physical properties at 25° have been quoted in our earlier communications.

The fluorocarbons show remarkable chemical and physical properties which illustrate the abnormally high intramolecular and low intermolecular forces in these compounds. Chemically, they are extremely inert, and do not react with concentrated acids, alkali, oxidising agents, or the majority of chemical reagents. Decomposition with potassium or sodium at 600—700° was used for analysis. Profound degradation occurs when fluorine is passed into a liquid fluorocarbon, but when the fluorine is diluted with nitrogen there is either no reaction or the reaction can be controlled to a certain extent. Perfluoromethyl*cyclo*hexane, for example, can be converted into perfluoro*cyclo*hexane in small yield by treatment with diluted fluorine, thus indicating that the initial attack takes place on the side chains and not on the nucleus. Impure fluorocarbons give polymeric as well as decomposition products. When a fluorocarbon is mixed with fluorine diluted by nitrogen and passed through a heated tube, degradation to fluorocarbons of lower molecular weight occurs. Reaction with cobalt trifluoride at high temperatures also brings about carbon–carbon bond fission. The fluorocarbons are thermally very stable, and perfluoromethyl*cyclo*hexane, for example, underwent little decomposition at 550°. Prolonged heating at 550—700° brought about partial decomposition to fluorocarbons of lower molecular weight with the deposition of carbon.

The effect of fluorine on the boiling point of a hydrocarbon is quite different from that observed with the other halogens. The introduction of one fluorine atom almost invariably raises boiling point, a notable exception being the replacement of nuclear hydrogen in an aromatic compound. Subsequent introduction of fluorine leads to a further increase in boiling point until a maximum is reached, after which the boiling points of the fluoro-derivatives steadily fall to a minimum when all hydrogen atoms have been replaced by fluorine and all double bonds saturated by fluorine (*e.g.*, methyl*cyclo*hexane, b. p. 101°, trifluoromethyl*cyclo*hexane, b. p. 107°, perfluoromethyl*cyclo*hexane, b. p. 76°). The boiling point of a fluorocarbon containing more than five carbon atoms is lower than that of the corresponding hydrocarbon and the difference in boiling point increases with higher members of the series. The boiling points of fluorocarbons are recorded in Table II. Those of isomeric fluorocarbons are very similar, and perfluoro-1 : 2-, -1 : 3-, and -1 : 4-dimethyl*cyclo*hexane and perfluoroethyl*cyclo*hexane, for example, all boil in the range 101—103°. It is not surprising to find that the empirical relationships which have been used to correlate the boiling point and structure of hydrocarbons (*e.g.*, Lautié, *Bull. Soc. chim.*, 1940, **7**, 685 : Nekraskov, *Z. physikal. Chem.*, 1929, *A*, **141**, 378 ; 1930, *A*,**148**, 216) hold equally well or even better for the fluorocarbons.

The introduction of fluorine into an organic compound gives a product of higher density than the starting material, and in this respect fluorine resembles the other halogens. The density–temperature graphs for the fluorocarbons (cf. Table III) are linear and almost parallel for the higher members of the series. The molecular volumes of the fluorocarbons calculated from extrapolated densities at the boiling point are shown in Table IV.

The refractive indices of the fluorocarbons are shown in Table V ; fluorine reduces the refractive index relative to the parent hydrocarbon. The refractive indices of the fluorocarbons are the lowest recorded for organic compounds of comparable complexity. The temperature coefficient for refractive index is approximately 0·0004 for all the fluorocarbons examined.

It appears that the specific refraction of a homologous series is characteristic and almost constant for the series—0·09625 for the perfluoroparaffins, 0·0971 for the monocyclic fluorocarbons, and 0·0997 for the bicyclic fluorocarbons (Table VI). The specific refraction is independent of temperature over the ranges measured.

The atomic refraction of fluorine is 1·220 for the mono- and bi-cyclic fluorocarbons; in the perfluoroparaffins, it slowly decreases with ascent of the series, with an average value of *ca.* 1·255 (Table VI, cf. Grosse and Cady, *loc. cit.*; Fowler *et al.*, *loc. cit.*). Thus the atomic refraction of fluorine varies with the type of compound. Henne (*J. Amer. Chem. Soc.*, 1936—1949), Grosse, Wackher, and Linn (*J. Physical Chem.*, 1940, **44**, 275) and Swarts (*J. Chim. physique*, 1923, **20**, 30) have found values of AR_F from 0·90 to 1·10 in diverse partially fluorinated paraffins.

If it is known to which homologous series (paraffin, monocyclic, or bicyclic) a partially fluorinated compound, $C_xH_yF_z$, containing only carbon, hydrogen, and fluorine belongs, then its degree of fluorination (the ratio of number of fluorine atoms to the total number of atoms other than carbon) can be estimated from measurements of refractive index and density, taking

AR_C = 2·418, AR_H = 1·100, and the appropriate value for AR_F. The procedure can be extended to the relation between specific refraction and degree of halogenation for chlorofluorohydrocarbons. Refractometric analysis of this type is most accurate for compounds with a high degree of halogenation and is particularly useful in estimating the hydrogen content of the compound.

The viscosities of the fluorocarbons are greater than those of the corresponding hydrocarbons but very much less than those of chlorinated compounds with a similar degree of halogenation. The large change in viscosity with temperature for the fluorocarbons (see Tables VII and VIII) again indicates the low order of magnitude of the intermolecular forces. The fluidity ($1/\eta$)–temperature curves tend to linearity at higher temperatures but, when log η is plotted against the reciprocal of absolute temperature, a more strictly linear relationship is found. The variation of viscosity with temperature for the fluorocarbons may therefore be represented by an equation of the type $\log \eta = B/T - A$, which is equivalent to the expression $\eta = C/Ke^{RT}$ derived by Andrade (*Phil. Mag.*, 1934, **17**, 497, 698) where K and C are constants. Values of A and B are recorded in Table IX. It is interesting that there is a marked difference in viscosity between a perfluoroparaffin and a mono- or bi-cyclic compound with the same number of carbon atoms. This is particularly noticeable at the lower temperatures (*e.g.*, C_7F_{14} shows η^{25} 15·6 while C_7F_{16} shows η^{25} 9·15; $C_{10}F_{18}$ shows η^{25} 51·4 while $C_{10}F_{20}$ has η^{25} 29·5). Molecular structure is clearly a major factor in determining viscosity and consequently viscosity can be used to distinguish fluorocarbons having the same number of carbon atoms but different carbon skeletons.

Introduction of one fluorine atom into a hydrocarbon causes an increase in the surface tension. Further fluorination causes initially an increase, and later a decrease, in the surface tension, and in this respect the change in surface tension is analogous to the change produced in the boiling point by progressive fluorination (*e.g.*, γ^{20} for C_6H_{14} 18·4, $C_6H_{13}F$ 21·8, $C_6H_5{\cdot}CH_3$ 28·5, $C_6H_5{\cdot}CF_3$ 23·4, $C_6F_{11}{\cdot}CF_3$ 14·2). The surface tensions of the fluorocarbons are lower than those of other organic compounds of a similar molecular complexity and vary linearly with temperature (see Table X).

The parachors of the fluorocarbons vary only slightly ($\pm$ 0·5%) with temperature, the maximum deviation occurring as might be expected at temperatures near the boiling point.

The average value of P_{CF_2} (see Table XI) for the perfluoroparaffins and the perfluoro-cyclic compounds is 53·7, whence P_F is 22·55. The values of P_F in Table XI calculated by assuming that there is no constitutional parachor for the ring systems show that there is good agreement within a particular homologous series with only slight differences between the alicyclic, monocyclic, and bicyclic compounds.

The value of P_F derived from the fluorocarbons is much lower than any previously put forward from measurements on other organic fluorides. Sugden ("Parachor and Valency") suggested 25·0 and Mumford and Phillips (*J.*, 1929, 2112) 25·5, while Desreux (*Bull. Soc. chim. Belg.*, 1935, **44**, 249) used 26·3, 24·2, or 25·1 when fluorine was present in an aliphatic, trifluoromethyl, or an aromatic compound respectively.

EXPERIMENTAL.

Purification of Fluorocarbons.—The crude fluorocarbons obtained by the methods described in Parts III—V were extracted with cold absolute ethanol to remove fluorohydrocarbons, and after being washed with water and dried were either passed over cobalt trifluoride at 350° or, more usually, treated with uranium hexafluoride at 100°, at the boiling point or under pressure. After removal of uranium hexafluoride, washing, and drying, the fluorocarbons were distilled through an efficient fractionating column. Middle fractions were taken for the measurement of physical properties, each of which is the average of at least two determinations with fresh samples.

Chemical Properties of the Fluorocarbons.—Only typical experiments are described.

Reaction with acids. Perfluorodimethyl*cyclo*hexane (30 g.) did not react with concentrated sulphuric acid (100 ml.) during 5 hours at room temperature or later during 4 hours under reflux. Similar results were observed with fuming nitric acid, concentrated potassium permanganate solution, or chromic acid.

Reaction with alkali. Perfluorononane (25 g.) was unaffected overnight by 50% sodium hydroxide solution or when later heated under reflux for 5·5 hours.

Reaction with fluorine in the liquid phase. After perfluorodimethyl*cyclo*hexane (30 g.), stirred rapidly, had been treated with fluorine (5 g./hr.) diluted with nitrogen (10 l./hr.) for 5 hours, the residue (22·1 g.) was mainly unchanged, with a trace of more volatile material.

Perfluoromethyl*cyclo*hexane (21 g.) treated with fluorine (10 g./hr.) diluted with nitrogen (7 l./hr.) yielded perfluoro*cyclo*hexane (0·2 g.), unchanged perfluoromethyl*cyclo*hexane (14·2 g.), and volatile products. Impure fluorocarbons gave polymeric as well as decomposition products on treatment with fluorine diluted with nitrogen, whilst the passage of undiluted fluorine into fluorocarbons caused inflammation and some deposition of carbon.

Reaction with fluorine in the vapour phase. Perfluorodimethyl*cyclo*hexane and fluorine (diluted by equal volume of nitrogen) were introduced through diametrically opposite tubes in a horizontal unpacked steel reaction vessel 34″ long and 3″ in diameter, and the products condensed and distilled. The results are summarised in Table I.

TABLE I.

Temp.	50°	50°	100°	120°	160°
C_8F_{16} (ml./hr.)	4	2	3	2·5	2
F_2 (g./hr.)	6	5	5	7	8
C_8F_{16} recovered, %	74	60	62	52	34

Reaction with cobalt trifluoride. Perfluorononane (21·0 g.) was passed over cobalt trifluoride at 550° to yield material (8·4 g.) of b. p. $<125°$ produced by decomposition.

Reaction in a hot tube. Perfluoromethyl*cyclo*hexane was passed rapidly through a nickel tube furnace at 550° with no change in physical properties. Prolonged heating at this temperature caused partial decomposition with deposition of carbon. Carbon tetrafluoride was the main decomposition product although small amounts (*ca.* 10%) of C_2F_6, C_3F_8, etc., were also present.

Boiling Point, Melting Point, and Freezing Point.—Accurate and corrected b. p.s and approx. f. p.s are recorded in Table II. Perfluoro-decane, -undecane, -dodecane, and -hexadecane were recrystallised from carbon tetrachloride.

TABLE II.

Fluoroparaffin.	C_7F_{16}.	C_8F_{18}.	C_9F_{20}.	$C_{10}F_{22}$.	$C_{11}F_{24}$.	$C_{12}F_{26}$.	$C_{16}F_{34}$.
B. p.	82·2°	103·3°	125·3°	144·2°	161°	178°	232°
M. p. or f. p.	−55°	−65°	−16°	36°	57°	75°	125°
Monocyclic.	C_6F_{12}.	C_7F_{14}.	C_8F_{16}.	C_9F_{18}.	$C_{10}F_{20}$.		
B. p.	52·0°	76·2°	101·5°	124·6°	146·5°		
M. p. or f. p.	51°	−37°	−55°	−56°	−44°		
Dicyclic.	$C_{10}F_{18}$.	$C_{11}F_{20}$.					
B. p.	141·9°	160·5°					
M. p. or f. p.	−14°	−40°					

Application of Lautié's expression (*loc. cit.*), $T_b^2 = An + B$ [where T_b is the boiling point (°K.), A and B are constants, and n is the number of carbon atoms in the compound] to the perfluoroparaffins gives $A = 15{,}400$ and $B = 19{,}000$, and satisfactory agreement with the experimental values. The mono- and bi-cyclic fluorocarbons have $A = 18{,}000$ $B = -3{,}900$, and $A = 15{,}800$, $B = 14{,}000$ respectively.

Nekrasov's expression (*loc. cit.*), which can be reduced to that of Lautié, can also be applied with some success to the fluorocarbons. In this equation, $T_b = KM^{1\cdot5}/R$, where K is a constant, M is the molecular weight, and R is the molecular refraction, use of 2·418 and 1·220 (see Table V) for the atomic refraction of carbon and fluorine respectively, leads to a value of $1\cdot700 \pm 0\cdot006$ for K for the perfluoroparaffins. The expression may then be used to calculate the b. p.s of the fluorohydrocarbons, but the absence of data for fully-characterised fluorohydrocarbons prevents comparison of calculated and observed values.

Density.—Standard methods were used with pyknometers of *ca.* 6·5-ml. and 1·5-ml. capacity. Water- and liquid paraffin-thermostats were used, with temperature control to $\pm 0\cdot05°$. Readings were taken at 5 or 6 temperatures in the range indicated in each case and showed a linear relationship between density and temperature. The results are most conveniently recorded therefore in the form $d_4^T = A - BT$ where A and B are constants and T is the temperature (°C.). The data are recorded in Table III. Values of 0·0023 and 0·0027 g./c.c. deg. for the value $B(\mathrm{d}d/\mathrm{d}T)$ have been recorded by Cady *et al.* (*loc. cit.*) for perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane and perfluoro-*n*-heptane respectively.

Kopp suggested that the molecular volumes of hydrocarbons calculated from the densities at the b. p.s are additive in character, and derived a value of 11·0 for the molecular volume of carbon. The molecular

TABLE III.

	A.	*B.*	Temp. range.		*A.*	*B.*	Temp. range.
Monocyclic.				*Fluoroparaffin.*			
C_7F_{14}	1·858	0·00284	0—60°	C_7F_{16}	1·801	0·00240	0—60°
C_8F_{16}	1·897	0·00271	0—60	C_8F_{18}	1·839	0·00251	0—60
C_9F_{18}	1·948	0·00231	0—60	C_9F_{20}	1·860	0·00248	0—60
$C_{10}F_{20}$	1·959	0·00231	0—60	$C_{10}F_{22}$	1·873	0·00230	35—60
				$C_{11}F_{24}$	1·919	0·00248	60—130
Dicyclic.				$C_{12}F_{26}$	1·961	0·00256	80—175
$C_{10}F_{18}$	1·979	0·00232	0—70				
$C_{11}F_{20}$	2·001	0·00222	0—70				

volumes of the fluorocarbons shown in Table IV are calculated from the densities at the b. p.s derived by extrapolation from the data in Table III. The plots of molecular volume at the b. p. against the number of carbon atoms in the fluorocarbon are slightly curved for the perfluoroparaffins and cyclic fluorocarbons, and the molecular volume of fluorine, calculated on the assumption that the molecular volume of carbon in these compounds is 11·0, increases from 10·3 to 11·7 and from 9·5 to 9·9 in the two series. Substantial errors may be involved in the extrapolation to the b. p. of the density–temperature curves.

Refractive Index.—The refractive indices of the fluorocarbons are recorded in Table V in the form $n_D{}^T = A - BT$ where T is in °c. The refractive index was measured at 10—15 different temperatures in each case. An Abbé refractometer with a special scale was used, and gave readings accurate to $\pm$0·0005 in the region below 1·3000. The value of dn_D/dT is *ca.* —0·00040 for all the fluorocarbons examined.

TABLE IV.

Compound.	C_7F_{16}	C_8F_{18}.	C_9F_{20}.	$C_{10}F_{22}$.	$C_{11}F_{24}$.	$C_{12}F_{26}$.
Mol. vol. at b. p.	242·1	277·2	314·9	350·8	387·5	425·0
Compound.	C_7F_{14}.	C_8F_{16}.	C_9F_{18}.	$C_{10}F_{20}$.	$C_{10}F_{18}$.	$C_{11}F_{20}$.
Mol. vol. at b. p.	213·3	242·2	271·2	308·7	280·8	311·5

TABLE V.

	A.	*B*.	Temp. range.		*A*.	*B*.	Temp. range.
Monocyclic.				*Fluoroparaffin.*			
C_7F_{14}	1·2865	0·00042	0—40°	C_7F_{16}	1·2770	0·00040	0—40°
C_8F_{16}	1·2935	0·00042	0—60	C_8F_{18}	1·2820	0·00040	0—40
C_9F_{18}	1·3035	0·00038	0—70	C_9F_{20}	1·2865	0·00042	0—50
$C_{10}F_{20}$	1·3060	0·00038	0—65	$C_{10}F_{22}$	1·2890	0·00040	35—60
				$C_{11}F_{24}$	1·2960	0·00040	60—80
Dicyclic.							
$C_{10}F_{18}$	1·3185	0·00040	0—70				
$C_{11}F_{20}$	1·3215	0·00038	0—70				

TABLE VI.

	r.	$[M_E]$.	AR_F.		*r*.	$[M_E]$.	AR_F.
Monocyclic.				*Fluoroparaffin.*			
C_7F_{14}	0·09694	33·93	1·214	C_8F_{18}	0·09618	42·13	1·266
C_8F_{16}	0·09712	38·86	1·220	C_9F_{20}	0·09621	46·21	1·259
C_9F_{18}	0·09714	43·71	1·220	$C_{10}F_{22}$	0·09625	51·78	1·255
$C_{10}F_{20}$	0·09721	48·61	1·221	$C_{11}F_{24}$	0·09634	56·65	1·252
Dicyclic.							
$C_{10}F_{18}$	0·0998	46·14	1·220				
$C_{11}F_{20}$	0·0997	51·00	1·220				

The values for the specific refraction *r* shown in Table VI have been calculated from the Lorentz–Lorenz expression using n_D^{25}, the molecular refraction $[M_E]$ and the atomic refraction of fluorine AR_F were derived by using the Eisenlohr value of 2·418 for the atomic refraction of carbon.

The values of n_D^{25} and d_4^{25} for $C_{10}F_{22}$ and $C_{11}F_{24}$ were extrapolated. Fowler *et al.* (*loc. cit.*) quote a value for AR_F of 1·24—1·25 for both perfluoroparaffins and perfluoromonocyclic hydrocarbons.

Viscosity.—The viscosity (millipoises) of the fluorocarbons, determined in standard Ostwald viscometers, are recorded in Tables VII and VIII. The variation in viscosity with temperature is conveniently expressed in the form $\log \eta = (B/T) - A$ and values of B and A are recorded in Table IX.

TABLE VII.

Temp. :	25°.	30°.	35°.	45°.	60°.	70°.	80°.	90°.
Monocyclic.								
C_7F_{14}	15·6	14·1	12·8	10·6	8·11	6·98	—	—
C_8F_{16}	19·3	17·4	15·8	13·2	10·2	—	—	—
C_9F_{18}	22·4	20·0	18·3	15·1	11·7	—	—	—
$C_{10}F_{20}$	29·5	26·1	23·3	18·6	13·5	—	—	—
Dicyclic.								
$C_{10}F_{18}$	51·4	42·9	37·6	28·6	19·6	15·8	12·6	—
$C_{11}F_{20}$	53·6	—	39·9	30·6	20·7	16·8	13·4	11·0

Surface Tension and Parachor.—The surface tension was determined by Sugden's maximum bubble-pressure method (*J.*, 1922, 864; *J.*, 1924, 27), improved according to Quayle and Smart (*J. Amer. Chem. Soc.*, 1944, **66**, 937; 1945, **67**, 21) and by Desreux (*loc. cit.*). The surface tensions of the fluorocarbons are extremely low, and precautions were taken to exclude dust, grease, etc. Where possible a different and freshly distilled sample of the fluorocarbon was used for each determination. The surface tension of each fluorocarbon was determined for at least five different temperatures. In each case the surface tension varied linearly with temperature and is best expressed in the form $\gamma_T = \gamma_0 - KT$, where γ_0 is the surface tension at 0° and T is the temperature in °c., which must be above the m. p. of the compound. Values of γ_0 (dynes/cm.) and K are shown in Table X. The values of γ_0 for $C_{10}F_{22}$, $C_{11}F_{24}$, and $C_{12}F_{16}$ have been derived by extrapolation.

TABLE VIII.

Temp. :	25°.	30°.	35°.	45°.	60°.	70°.	80°.	85°.	90°.	95°.
Perfluoroparaffins.										
C_7F_{16}	9·15	8·31	7·69	6·61	—	—	—	—	—	—
C_8F_{18}	14·9	13·6	12·4	10·4	8·12	7·07	—	—	—	—
C_9F_{20}	18·1	16·3	14·7	12·2	9·15	—	—	—	—	—
$C_{10}F_{22}$	—	—	20·5	16·4	12·0	10·0	8·37	—	—	—
$C_{11}F_{24}$	—	—	—	—	16·4	13·5	11·1	—	9·38	—
$C_{12}F_{26}$	—	—	—	—	—	—	13·1	11·9	10·8	10·0

TABLE IX.

Fluorocarbon.	C_7F_{16}.	C_8F_{18}.	C_9F_{20}.	$C_{10}F_{22}$.	$C_{11}F_{24}$.	$C_{12}F_{26}$.
B	641·8	733·2	839·7	938·3	976·1	1001
A	1·1978	1·2871	1·5602	1·7351	1·7167	1·7195

Fluorocarbon.	C_7F_{14}.	C_8F_{16}.	C_9F_{18}.	$C_{10}F_{20}$.	$C_{10}F_{18}$.	$C_{11}F_{20}$.
B	775·0	763·0	782·1	940·8	1147	1127
A	1·4142	1·2800	1·2804	1·6889	2·1478	2·0588

TABLE X.

Fluorocarbon.	C_7F_{14}.	C_8F_{16}.	C_9F_{18}.	$C_{10}F_{20}$.	$C_{10}F_{18}$.	$C_{11}F_{20}$.
γ_0	15·85	17·02	19·10	19·57	20·36	21·17
K	0·0840	0·0806	0·0774	0·0814	0·0834	0·0804

Fluorocarbon.	C_8F_{18}.	C_9F_{20}.	$C_{10}F_{22}$.	$C_{11}F_{24}$.	$C_{12}F_{26}$.
γ_0	15·52	16·34	16·68	17·47	18·23
K	0·0711	0·0766	0·0700	0·0665	0·0665

TABLE XI.

Fluorocarbon.	C_7F_{14}.		C_8F_{16}.		C_9F_{18}.		$C_{10}F_{20}$.		$C_{10}F_{18}$.		$C_{11}F_{20}$.
P	377·3		431·4		484·9		538·1		497·1		550·8
P_{CF_2}		53·2		53·5		54·1				53·7	
P_F	22·65		22·66		22·64		22·61		22·83		22·81

Fluorocarbon.	C_8F_{18}.		C_9F_{20}.		$C_{10}F_{22}$.		$C_{11}F_{24}$.		$C_{12}F_{26}$.
P	474·7		528·4		582·5		636·3		690·0
P_{CF_2}		53·7		54·1		53·8		53·7	
P_F	22·55		22·55		22·57		22·57		22·57

The parachors (P) of the fluorocarbons, the increment in parachor for a $-CF_2-$ group (P_{CF_2}) for successive members of a homologous series, and the atomic parachor of fluorine (P_F) calculated from the above data are shown in Table XI. The atomic parachor of carbon was taken as 8·6, the value derived by Vogel *et al.* (*J.*, 1934, 333; 1943, 636; 1946, 133).

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