Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINATED ALIPHATIC COMPOUNDS

The hydrogen atoms in alkanes can be partially or completely replaced by fluorine. Partially fluorinated alkanes are commonly called hydrofluorocarbons (HFCs) and the fully fluorinated derivatives are perfluorocarbons (PFCs). Alkanes whose hydrogens are replaced by both fluorine and chlorine are designated chlorofluorocarbons (CFCs), or hydrochlorofluorocarbons (HCFCs) if the replacement is incomplete. Similar designations are used for other halogenated fluorocarbons. Fluorinated aliphatics are further identified by a series of numbers related to the formula of the compound. In this numbering system for methane and ethane derivatives, the first digit on the right is the number of fluorine atoms in the compound, and the second digit from the right is one more than the number of hydrogen atoms. The third digit from the right is one less than the number of carbon atoms, but when this digit is zero, it is omitted. The remaining available positions in the compound are taken by chlorine atoms unless specified otherwise. For example, CCl_3F, $CHClF_2$, CF_3CHF_2, and CF_3CF_3 are designated CFC-11, HCFC-22, HFC-125, and PFC-116, respectively. When bromine is present, the same rules apply except that the letter B is used, followed by a number that indicates the number of chlorine atoms replaced by bromine. For example, CF_3Br and $CHBrF_2$ are coded BFC-13B1 and HBFC-22B1, respectively. In the fire extinguishing trade, the brominated derivatives are usually called Halons and have a different numbering system in which the digits from right to left are respectively the number of bromine, chlorine, fluorine, and carbon atoms. Any remaining available positions are hydrogen atoms. The above BFC and HBFC become H-1301 and H-1201 in this system. This numbering system has been extended systematically to both acyclic and cyclic compounds with more than two carbon atoms, but the code for distinguishing various isomers becomes rather complex (1).

1. Perfluorocarbons and Hydrofluorocarbons

1.1. Properties

Aliphatic PFCs have an unusual combination of physical properties relative to their hydrocarbon counterparts (2–5). The volatilities of PFCs are much higher than expected based on their molecular weights. For example, tetrafluoromethane, mol wt 88, boils at $-128°C$, whereas n-hexane, mol wt 86, boils at $+69°C$. Perfluorocarbons containing up to four carbon atoms boil somewhat higher than the corresponding hydrocarbons; the reverse is true of PFCs with more carbon atoms. Liquid PFCs are two to three times as dense as hydrocarbons with the same carbon skeleton, and aliphatic PFCs have among the lowest dielectric constants, refractive indexes, and surface tensions of any liquids at room temperature. The compressibilities and absolute viscosities of PFCs are considerably higher than those of hydrocarbons. Aliphatic PFCs are poor solvents for all materials except for those with low cohesive energies, such as gases and other PFCs. They are practically insoluble in water and only slightly soluble in hydrocarbons.

The extremely nonpolar character of PFCs and very low forces of attraction between PFC molecules account for their special properties. Perfluorocarbons boil only slightly higher than noble gases of similar

Table 1. Physical Properties of Aliphatic Perfluorocarbons (PFCs)[a]

PFC number	Formula	CAS Registry Number	Molecular weight	Boiling point, °C	Melting point, °C	Liquid density, g/mL at °C	Liquid refractive index, n_D at °C	Critical temp, °C	Critical pressure, MPa[b]
14	CF_4	[75-73-0]	88.01	−128.1	−183.6	1.613_{-130}	1.151_{-73}	−45.6	3.74
116	CF_3CF_3	[76-16-4]	138.02	−78.2	−100.6	1.600_{-80}	1.206_{-73}	19.7	2.99
218	$CF_3CF_2CF_3$	[76-19-7]	188.03	−36.7	−183	1.350_{20}		71.9	2.68
31-10	$CF_3(CF_2)_2CF_3$	[355-25-9]	238.04	−2.2	−128	1.543_{20}		113.2	2.32
C-318	cyclo-C_4F_8	[115-25-3]	200.04	−5.9	−41.4	1.500_{25}	1.217_{25}	115.2	2.78
41-12	$CF_3(CF_2)_3CF_3$	[678-26-2]	288.05	29.2	−126	1.620_{20}	1.242_{15}	149	2.04
51-14	$CF_3(CF_2)_4CF_3$	[355-42-0]	338.07	58	−86	1.680_{25}	1.251_{22}	174.5	1.90
61-16	$CF_3(CF_2)_5CF_3$	[335-57-9]	388.08	82.5	−51	1.733_{20}	1.262_{20}	201.6	1.62
PP3[c]	cyclo-$C_6F_{10}(CF_3)_2$[d]	[335-27-3]	400.09	102	−70	1.828_{25}	1.290_{25}	241.5	1.88
PP6[c]	cyclo-$C_{10}F_{18}$[e]	[306-94-5]	462.11	142	[f]	1.917_{25}	1.313_{25}	292.0	1.75
PP9[c]	cyclo-$C_{10}F_{17}(CF_3)$[g]	[306-92-3]	512.12	160	−70	1.972_{25}	1.320_{25}	313.4	1.66
PP11[c]	cyclo-$C_{14}F_{24}$[h]	[306-91-2]	624.15	215	−20	2.03_{25}	1.335_{25}	377[i]	1.46[i]

[a] Refs. (6–8).
[b] To convert MPa to psi, multiply by 145.
[c] Flutec number (trademark of Rhône-Poulenc, Inc., RTZ Chemicals, ISC Division).
[d] Perfluoro-1,3-dimethylcyclohexane.
[e] Perfluorodecalin, *cis/trans* mixture.
[f] −11.2 to 18.0°C, depending on cis/trans ratio.
[g] Perfluoro-2-methyldecalin.
[h] Perfluorotetradecahydrophenanthrene.
[i] Estimated values.

molecular weight, and their solvent properties are much more like those of argon and krypton than hydrocarbons (2). The physical properties of some PFCs are listed in Table 1.

The physical properties of hydrofluorocarbons reflect their polar character, and possibly the importance of intermolecular hydrogen bonding (3). Hydrofluorocarbons often boil higher than either their PFC or hydrocarbon counterparts. For example, 1-$C_6H_{13}F$ boils at 91.5°C compared with 58°C for n-C_6F_{14} and 69°C for n-C_6H_{14}. Within the series of fluorinated methanes, the boiling point reaches a maximum for CH_2F_2, which contains an equal number of hydrogen and fluorine atoms for maximum hydrogen bonding. The methane boiling points, however, also parallel their dipole moments, which reflect relative polar character: CH_3F ($\mu = 1.85D$), CH_2F_2 (1.97D), CHF_3 (1.65D), CF_4 (0.0D) ($1D = 3.336 \times 10^{-30} C{\cdot}m$).

Hydrofluorocarbons invariably have higher refractive indexes, dielectric constants, and surface tensions, but lower densities than their PFC counterparts. The physical properties of some HFCs are listed in Table 2. Because of their very strong carbon–fluorine and carbon–carbon bonds (10), the chemical and thermal stability of PFCs is considerably higher in general than that of the corresponding hydrocarbons (3, 11). Perfluorocarbons normally are significantly less reactive than hydrocarbons toward all chemical reagents except alkali metals. Molten alkali metals or alkali–metal hydrocarbon complexes degrade most fluorocarbons, and this reaction is used for their chemical analysis (3). Perfluorocarbons are not affected by acids or oxidizing agents and are not hydrolyzed below 500°C. Carbon tetrafluoride decomposes only slowly at carbon arc temperatures, and it does not react with Cu, Ni, W, or Mo at 900°C. Perfluorocarbons of higher molecular weight are less thermally stable, but temperatures approaching 1000°C are still required to decompose C_2F_6 or n-C_3F_8, and most PFCs are stable below 300°C. Partially fluorinated hydrocarbons are less stable and more reactive, especially when

Table 2. Physical Properties of Aliphatic Hydrofluorocarbons (HFCs)[a]

HFC number	Formula	CAS Registry Number	Molecular weight	Boiling point, °C	Melting point, °C	Liquid density, g/mL at °C	Liquid refractive index, n_D at °C	Critical temp, °C	Critical pressure, MPa[b]
23	CHF_3	[75-46-7]	70.01	−82.2	−155.2	1.442_{-80}	1.215_{-73}	25.7	4.83
32	CH_2F_2	[75-10-5]	52.02	−51.6	−136	1.200_{-50}	1.190_{20}		
41	CH_3F	[593-53-3]	34.03	−78.3	−141.8	0.884_{-80}	1.1727_{20}	44.6	5.86
125	CHF_2CF_3	[354-33-6]	120.02	−48.5	−103	$1.53_{-48.5}$	1.5012_{19}	72.4	3.52
134	CHF_2CHF_2	[359-35-3]	102.03	−19.7	−89		1.250_{20}		
134a	CH_2FCF_3	[811-97-2]	102.03	−26.5	−101	1.21_{25}		101.1	4.14
143	CHF_2CH_2F	[430-66-0]	84.04	5.0	−84			71.2	
143a	CH_3CF_3	[420-46-2]	84.04	−47.4	−111.3	1.176_{-50}	1.22_{25}	73.1	3.76
152	CH_2FCH_2F	[624-72-6]	66.05	30.7		0.913_{19}	1.28_{25}	107.5	
152a	CH_3CHF_2	[75-37-6]	66.05	−25.8	−117	1.023_{-30}	1.3011_{-72}	113.5	4.50
161	CH_3CH_2F	[353-36-6]	48.06	−37.4	−143.2	0.818_{-37}	1.3033_{-37}	102.2	4.72
227ea	CF_3CFHCF_3[c]	[431-89-0]	170.03	−18	−129.5	1.407_{25}		101.7	2.91
245ca	$CHF_2CF_2CH_2F$	[679-86-7]	134.05	26	−82		1.30_{15}		
245cb	$CF_3CF_2CH_3$	[1814-88-6]	134.05	−18				106.9	
254fb	$CH_2FCH_2CF_3$	[460-36-6]	116.06	29.4		1.2584_{25}	1.2765_{25}		
272ca	$CH_3CF_2CH_3$	[420-45-1]	80.08	−0.4	−104.8	0.9205_{20}	1.2904_{20}		
272fa	$CH_2FCH_2CH_2F$	[462-39-5]	80.08	41.6		1.0057_{25}	1.3190_{26}		
281ea	CH_3CHFCH_3	[420-26-8]	62.09	−10	−133.4	0.7238_{-20}	1.3075_{-10}		
281fa	$CH_2FCH_2CH_3$	[460-13-9]	62.09	−2.5	−159	0.7956_{20}	1.3115_{20}		

[a] Refs. (5, 7–9).

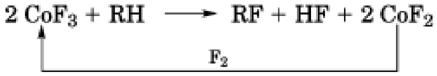
[b] To convert MPa to psi, multiply by 145.

[c] Unpublished data, Great Lakes Chemical Co.

only one fluorine atom is present. Hydrogen fluoride can be eliminated by chemical or thermal action from hydrofluorocarbons.

1.2. Manufacture

The direct fluorination of hydrocarbons with elemental fluorine is extremely exothermic and difficult to control. Special methods including metal packing techniques, jet reactors, and high dilution have been developed to control the reaction, but currently they have limited industrial importance (12). Poly(carbon monofluoride), $(CF)_x$, is one product that is made commercially by direct fluorination (of graphite) (13). The disadvantages of direct fluorination have been overcome by the use of fluorine carriers, in particular, high valence metal fluorides such as cobalt trifluoride, CoF_3, or potassium tetrafluorocobaltate, $KCoF_4$. These reagents replace hydrogen and halogen atoms by fluorine and add fluorine to double bonds and aromatic systems (12).



Cobalt trifluoride is generated *in situ* by passing fluorine over cobalt difluoride contained in a horizontal, mechanically agitated steel reactor. The compound to be fluorinated is passed through the reactor at 150–300°C as a vapor in a stream of nitrogen. After the reaction is completed, the CoF_3 is regenerated by adding fluorine. Advances in process control technology have allowed the process to be run continuously by simultaneously introducing the fluorine and hydrocarbon into the cobalt fluoride bed (6). Principally, cyclic and higher molecular weight acyclic fluorocarbons are prepared by this method.

Fluorocarbons are made commercially also by the electrolysis of hydrocarbons in anhydrous hydrogen fluoride (Simons process) (14). Nickel anodes and nickel or steel cathodes are used. Special porous anodes improve the yields. This method is limited to starting materials that are appreciably soluble in hydrogen fluoride, and is most useful for manufacturing perfluoroalkyl carboxylic and sulfonic acids, and tertiary amines. For volatile materials with little solubility in hydrofluoric acid, a complementary method that uses porous carbon anodes and $HF{\cdot}2KF$ electrolyte (Phillips process) is useful (14).

Hydrofluorocarbons are also prepared from acetylene or olefins and hydrogen fluoride (3), or from chlorocarbons and anhydrous hydrogen fluoride in the presence of various catalysts (3, 15). A commercial synthesis of 1,1-difluoroethane, a CFC alternative and an intermediate to vinyl fluoride, is conducted in the vapor phase over an aluminum fluoride catalyst.

$$HC{\equiv}CH + 2\,HF \xrightarrow{\text{catalyst}} CH_3CHF_2$$

$$CH_3CHF_2 + \text{heat} \longrightarrow CH_2{=}CHF + HF$$

Perfluorocyclobutane is prepared by the thermal cyclodimerization of tetrafluoroethylene [116-14-3].

1.3. Health and Safety Factors

Completely fluorinated alkanes are essentially nontoxic (16). Rats exposed for four hours to 80% perfluorocyclobutane and 20% oxygen showed only slight effects on respiration, but no pathological changes in organs. However, some fluorochemicals, especially functionalized derivatives and fluoroolefins, can be lethal. Monofluoroacetic acid and perfluoroisobutylene [382-21-8] are notoriously toxic (16).

1.4. Uses

The chemical inertness, thermal stability, low toxicity, and nonflammability of PFCs coupled with their unusual physical properties suggest many useful applications. However, the high cost of raw materials and manufacture has limited commercial production to a few, small-volume products. Carbon tetrafluoride and hexafluoroethane are used for plasma, ion-beam, or sputter etching of semiconductor devices (17) (see Ion implantation). Hexafluoroethane and octafluoropropane have some applications as dielectric gases, and perfluorocyclobutane is used in minor amounts as a dielectric fluid. Perfluoro-1,3-dimethylcyclohexane is used as an inert, immersion coolant for electronic equipment, and perfluoro-2-methyldecalin is used for pin-hole leak testing of encapsulated electronic devices (6, 18). Perfluoroperhydrophenanthrene has several diverse applications, ranging from a vapor-phase soldering agent for fabrication of printed circuits to a substitute for internal eye fluid in remedial eye surgery (6, 19).

Medical applications of PFC emulsions for organ perfusion and intravenous uses have received much attention in recent years. The first commercial blood substitute (Fluosol DA 20%, trademark of the Green Cross Corp.) employed perfluorodecalin, and improved, second generation products based on this PFC, or perfluorooctylbromide, are now under development (20, 21). The relatively high oxygen dissolving capability of PFCs underlies these applications (see Blood, artificial).

Poly(carbon monofluoride) is used as a high temperature lubricant and as a cathode material in high energy lithium batteries (13), but the fluorocarbons of greatest commercial interest and volume are the high molecular weight fluoroplastics and elastomers derived from tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride, and vinyl fluoride (22). Poly(tetrafluoroethylene) [9002-84-0], Teflon (trademark of E. I. du Pont de Nemours & Co.), and its copolymer [25067-11-2] with hexafluoropropylene, Teflon FEP, are fluorinated plastics, particularly notable for their outstanding chemical and thermal stability, electrical inertness, and

Table 3. Physical Properties of Aliphatic Chlorofluorocarbons (CFCs)[a]

CFC number	Formula	CAS Registry Number	Molecular weight	Boiling point, °C	Melting point, °C	Liquid density, g/mL at °C	Liquid refractive index, n_D at °C	Critical temp, °C	Critical pressure, MPa[b]
11	CCl_3F	[75-69-4]	137.36	23.8	−111	1.476_{25}	1.374_{25}	198.0	4.41
12	CCl_2F_2	[75-71-8]	120.91	−29.8	−158	1.311_{25}	1.287_{25}	112.0	4.11
13	$CClF_3$	[75-72-9]	104.46	−81.4	−181	1.298_{-30}	1.199_{-73}	28.9	3.87
111	CCl_3CCl_2F	[354-56-3]	220.29	137	100	1.740_{25}			
112	CCl_2FCCl_2F	[76-12-0]	203.82	92.8	26	1.634_{30}	1.413_{25}	278	3.44
112a	CCl_3CClF_2	[76-11-9]	203.82	91.5	40.6	1.649_{20}			
113	CCl_2FCClF_2	[76-13-1]	187.38	47.6	−35	1.565_{25}	1.354_{25}	214.1	3.41
113a	CCl_3CF_3	[354-58-5]	187.38	45.8	14.2	1.579_{20}	1.361_{20}		
114	$CClF_2CClF_2$	[76-14-2]	170.92	3.8	−94	1.456_{25}	1.288_{25}	145.7	3.26
114a	CCl_2FCF_3	[374-07-2]	170.92	3.6	−94	1.455_{25}	1.309_0	145.6	3.29
115	$CClF_2CF_3$	[76-15-3]	154.47	−39.1	−106	1.291_{25}	1.214_{25}	80.0	3.12

[a] Refs. (5, 7–9).

[b] To convert MPa to psi, multiply by 145.

nonflammability (23). Teflon has service temperatures in the range of −196 to 260°C. The copolymers [9011-17-0] of hexafluoropropylene and vinylidene fluoride, and the terpolymers [25190-89-0] of hexafluoropropylene, tetrafluoroethylene, and vinylidene fluoride (Viton fluoroelastomers, trademark of E. I. du Pont de Nemours & Co.) are rubbers with excellent thermal, chemical, and oxidative stability (24). They remain useful elastomers for indefinite periods of continuous exposure in air up to about 230°C (see Elastomers, synthetic–fluorocarbon elastomers).

2. Chlorofluorocarbons and Hydrochlorofluorocarbons

2.1. Properties

The physical properties of aliphatic fluorine compounds containing chlorine are similar to those of the PFCs or HFCs (3, 5). They usually have high densities and low boiling points, viscosities, and surface tensions. The irregularity in the boiling points of the fluorinated methanes, however, does not appear in the chlorofluorocarbons. Their boiling points consistently increase with the number of chlorines present. The properties of some CFCs and HCFCs are shown in Tables 3 and 4.

Although the CFCs and HCFCs are not as stable as the PFCs, they still can be rather stable compounds (3, 11). Dichlorodifluoromethane, CCl_2F_2, is stable at 500°C in quartz; CCl_3F and $CHClF_2$ begin to decompose at 450 and 290°C, respectively (7). The pyrolysis of $CHClF_2$ at 650–700°C in metal tubes is the basis of a commercial synthesis of tetrafluoroethylene:

$$2\ CHClF_2 + \text{heat} \longrightarrow CF_2{=}CF_2 + 2\ HCl$$

The chlorofluorocarbons react with molten alkali metals and CCl_2F_2 reacts vigorously with molten aluminum, but with most metals they do not react below 200°C. An exception is the dechlorination of chlorofluorocarbons with two or more carbon atoms in the presence of Zn, Mg, or Al in polar solvents. A commercial synthesis of chlorotrifluoroethylene [79-38-9] employs this reaction:

$$CClF_2CCl_2F + Zn \xrightarrow{\text{alcohol}} CF_2{=}CClF + ZnCl_2$$

Table 4. Physical Properties of Aliphatic Hydrochlorofluorocarbons (HCFCs)[a]

HCFC number	Formula	CAS Registry Number	Molecular weight	Boiling point, °C	Melting point, °C	Liquid density, g/mL at °C	Liquid refractive index, n_D at °C	Critical temp, °C	Critical pressure, MPa[b]
21	$CHCl_2F$	[75-43-4]	102.92	8.92	−135	1.366_{25}	1.354_{25}	178.5	5.17
22	$CHClF_2$	[75-45-6]	86.47	−40.75	−160	1.194_{25}	1.256_{25}	96.0	4.97
31	CH_2ClF	[593-70-4]	68.48	−9.1	−133	1.271_{20}			
121	$CHCl_2CCl_2F$	[354-14-3]	185.84	116.6	−82.6	1.622_{20}	1.4463_{20}		
121a	$CHClFCCl_3$	[354-11-0]	185.84	116.5	−95.4	1.625_{20}	1.4525_{20}		
122	$CClF_2CHCl_2$	[354-21-2]	169.39	71.9	−140	1.5447_{25}	1.3889_{20}		
122a	$CHClFCCl_2F$	[354-15-4]	169.39	72.5		1.5587_{20}	1.3942_{20}		
122b	CHF_2CCl_3	[354-12-1]	169.39	73		1.566_{20}	1.3979_{20}		
123	$CHCl_2CF_3$	[306-83-2]	152.93	28.7	−107	1.475_{15}	1.3332_{15}	185	3.79
123a	$CHClFCClF_2$	[354-23-4]	152.93	28.2	−78	1.498_{10}	1.327_{20}		
124	$CHFClCF_3$	[2837-89-0]	136.48	−12	−199	1.364_{25}		122.2	3.57
124a	CHF_2CClF_2	[354-25-6]	136.48	−10.2	−117	1.379_{20}			
131	$CHCl_2CHClF$	[359-28-4]	151.40	102.5		1.5497_{17}	1.4390_{20}		
131a	CH_2ClCCl_2F	[811-95-0]	151.40	88	−140.7	1.4227_{20}	1.4248_{20}		
132	$CHFClCHFCl$	[431-06-1]	134.94	59	−155	1.46_{20}	1.391_{20}		
132a	CHF_2CHCl_2	[471-43-2]	134.94	60		1.4945_{17}	$1.3830_{16.4}$		
132b	$CH_2ClCClF_2$	[1649-08-7]	134.94	46.8	−101	1.416_{20}	1.362_{20}	222	
133	$CHClFCHF_2$	[431-07-2]	118.49	17.2		1.365_{10}			
133a	CH_2ClCF_3	[75-88-7]	118.49	6.1	−105.5	1.389_{0}	1.309_{0}	153.0	
141	$CH_2ClCHClF$	[430-57-9]	116.95	75.7	−60	1.3814_{20}	1.4113_{20}		
141b	CCl_2FCH_3	[1717-00-6]	116.95	32	−103.5	1.2500_{10}	1.3600_{10}	210.3	4.640
142	CHF_2CH_2Cl	[338-65-8]	100.50	35.1		1.312_{15}	1.3528_{15}		
142a	$CHClFCH_2F$	[338-64-7]	100.50	35			1.3416_{20}		
142b	CH_3CClF_2	[75-68-3]	100.50	−9.2	−130.8	1.113_{25}		137.1	4.12
151	CH_2FCH_2Cl	[762-50-5]	82.50	53.2	<−50	1.1675_{25}	1.3752_{20}	237.6	
225ca	$CF_3CF_2CHCl_2$[c]	[422-56-0]	202.94	51.1	−94	1.55_{25}	1.326_{20}		
225cb	$CClF_2CF_2CHClF$[c]	[507-55-1]	202.94	56.1	−97	1.56_{25}	1.3262_{25}		

[a] Refs. (5, 7–9).

[b] To convert MPa to psi, multiply by 145.

[c] Physical data from Ref. 25.

Most chlorofluorocarbons are hydrolytically stable, CCl_2F_2 being considerably more stable than either CCl_3F or $CHCl_2F$. Chlorofluoromethanes and ethanes disproportionate in the presence of aluminum chloride. For example, CCl_3F and CCl_2F_2 give $CClF_3$ and CCl_4; $CHClF_2$ disproportionates to CHF_3 and $CHCl_3$. The carbon–chlorine bond in most chlorofluorocarbons can be homolytically cleaved under photolytic conditions (185–225 nm) to give chlorine radicals. This photochemical decomposition is the basis of the prediction that chlorofluorocarbons that reach the upper atmosphere deplete the earth's ozone shield.

2.2. Manufacture

The most important commercial method for manufacturing CFCs and HCFCs is the successive replacement of chlorine by fluorine using hydrogen fluoride (3, 15). The traditional, liquid-phase process uses antimony pentafluoride or a mixture of antimony trifluoride and chlorine as catalysts. Continuous vapor-phase processes that employ gaseous hydrogen fluoride in the presence of heterogenous chromium, iron, or fluorinated alumina catalysts also are widely used. Carbon tetrachloride, chloroform, and hexachloroethane (or tetrachloroethylene plus chlorine) are commonly used starting materials for one- and two-carbon chlorofluorocarbons. The extent

Table 5. Worldwide Production of Important Chlorofluorocarbons,[a] 10^3 t

Product	1986 Market	1991 Market	Percentage of 1986 market
CFC-11	415	263	63%
CFC-12	441	259	59%
CFC-113	241	143	59%
CFC-114	18	5	30%
CFC-115	13	11	85%

[a] Ref. 26.

Table 6. Worldwide Estimates of CFC Use by Industry, 1991 vs 1986[a]

Application	1986 Total uses, %	Reduction since 1986, %
propellants	28	58
refrigerants	23	7
cleaning	21	41
foam blowing agents	26	35
other uses	2	

[a] Ref. 26.

of chlorine exchange can be controlled by varying the hydrogen fluoride concentration, the contact time, or the reaction temperature.

$$CHCl_3 \xrightarrow{HF} CHCl_2F + CHClF_2 + CHF_3$$

$$CCl_4 \xrightarrow{HF} CCl_3F + CCl_2F_2 + CClF_3$$

$$CCl_3CCl_3 \xrightarrow{HF} CCl_2FCCl_3 + CCl_2FCCl_2F + CClF_2CCl_2F + CClF_2CClF_2$$

$$CH_3CCl_3 \xrightarrow{HF} CH_3CCl_2F + CH_3CClF_2 + CH_3CF_3$$

The direct chlorination of hydrofluorocarbons and fluoroolefins has also been used commercially, eg, in the preparations of CH_3CClF_2 from CH_3CHF_2 and $CClF_2CClF_2$ from tetrafluoroethylene.

2.3. Economic Aspects

The estimated worldwide production of important industrial CFCs is shown in Table 5. Trichlorofluoromethane, dichlorodifluoromethane, and trichlorotrifluoroethane account for over 95% of the total production. Between 1986 and 1991 the production of CFCs has decreased dramatically due to global adherence to the provisions of the Montreal Protocol and eventually will be phased out entirely. Estimates of the distribution by use in 1986 and subsequent reductions in use are shown in Table 6.

In 1990, approximately 115,000 t of CFCs were used as propellants, which represents a 58% decrease from the 1986 level. Most of this market segment likely will move to using hydrocarbon propellants, but the optimal choice of alternative will depend on the particular application. No suitable replacement for CFC-12 in pharmaceutical metered dose inhalers has been found. This single application represents a 6000 t/yr market. It also has been difficult to replace CFC-12 as the inert propellant for the potent sterilant ethylene oxide, which is a market for approximately 20,000 t per year.

Worldwide use of CFCs for refrigeration, air conditioning, and heat pumps totaled 260,000 t in 1991 (see Refrigeration) which is a dropoff of only 7% from 1986 levels.

Cleaning agent and solvent use has decreased 41% from 1986 levels, but in 1990, over 178,000 t of CFC-113 were still used in electronics, metal, precision, and dry cleaning (see Solvents, Industrial).

The use of CFCs as foam blowing agents has decreased 35% from 1986 levels. Polyurethanes, phenolics, extruded polystyrenes, and polyolefins are blown with CFCs, and in 1990 the building and appliance insulation markets represented about 88% of the 174,000 t of CFCs used in foams (see Foamed plastics).

2.4. Health and Safety Factors

The toxicity of aliphatic CFCs and HCFCs generally decreases as the number of fluorine atoms increases (16), as shown in Table 7, but there are exceptions as in the case of 141b vs 142b. Also, some derivatives like HCFC-132b can have low acute but high chronic toxicities (29).

2.5. Chlorofluorocarbons and Stratospheric Ozone Destruction

In 1971, it was shown (30) that CFCs were accumulating in the atmosphere, and three years later a relationship between CFCs and stratospheric ozone destruction, wherein the longlived CFCs that migrated to the upper stratosphere were being photolyzed by the intense uv radiation from the sun to form chlorine atoms, was proposed (31). These chlorine atoms then participated in an ozone destruction cycle, and it has been estimated that one chlorine atom destroys 10,000 ozone molecules before getting trapped as inactive HCl (32). Bromine also participates in a destruction cycle, but it is about 10 times more efficient than chlorine in destroying ozone (33).

The possibility that CFCs and Halons can deplete the earth's ozone layer has had a significant impact on the fluorochemicals industry. Also, CFCs have been cited as contributors to global warming owing to their absorption of infrared irradiation and long atmospheric lifetimes (34). Because aerosol products containing CFC-11 and CFC-12 had accounted for the biggest release of CFCs, their manufacture for this use was banned in 1978. The discovery of the Antarctic ozone hole in 1985 (35) has prompted the world community to take much more extensive action toward halting the release of CFCs.

2.6. The Montreal Protocol

In response to the growing scientific consensus that CFCs and Halons would eventually deplete the ozone layer, the United Nations Environmental Programme (UNEP) began negotiations in 1981 aimed at protecting the ozone layer. In March 1985, the Vienna Convention for the Protection of the Ozone Layer was convened and provided a framework for international cooperation in research, environmental monitoring, and information exchange. In September of 1987, the Montreal Protocol on Substances that Deplete the Ozone Layer was signed by 24 nations and took force on January 1, 1989. This treaty called for (*1*) limiting production of specified CFCs, including 11, 12, 113, 114, and 115, to 50% of 1986 levels by 1998, (*2*) freezing production of specified Halons 1211, 1301, and 2402 at 1986 levels starting in 1992, and (*3*) convening the signatories yearly to reevaluate and update the Protocol articles in light of recent developments. By 1988 the Ozone Trends Panel issued a report based on new scientific evidence that conclusively linked CFCs to ozone depletion in the stratosphere. In June of 1990, the parties to the Montreal Protocol met in London and amended the Protocol to strengthen the controls on ozone depleting chemicals, expand the list of chemicals to include carbon tetrachloride and

Table 7. Toxicity of Selected Halocarbons[a]

Compound	Formula	TLV,[b] ppm	ALC,[c] ppm
BFC-12B2	CBr_2F_2	100	7,102[d]
BCFC-12B1	$CBrClF_2$		131,000
BFC-13B1	$CBrF_3$	1000	800,000
HBCC-30B1	CH_2BrCl	200	28,800[e]
HBFC-22B1	$CHBrF_2$		108,000
CC-10	CCl_4	10	8,000
CFC-11	CCl_3F	1000	26,200
CFC-12	CCl_2F_2	1000	800,000
CFC-13	$CClF_3$	1000	>600,000[f]
HCC-20	$CHCl_3$	10[g]	8,861
HCFC-21	$CHCl_2F$	10	49,900
HCFC-22	$CHClF_2$	1000	220,000
HFC-23	CHF_3	1000[h]	>663,000
HCC-30	CH_2Cl_2	100	22,669[i]
CFC-113	CCl_2FCF_2Cl	1000	52,500
CFC-114	CF_2ClCF_2Cl	1000	720,000[i]
CFC-115	CF_3CF_2Cl	1000	>800,000
HCFC-123	CF_3CHCl_2	10[h]	32,000
HCFC-124	CF_3CHFCl	500[h]	>230,000
HFC-125	CF_3CF_2H	1000[h]	>709,000
HFC-134a	CF_3CH_2F	1000[h]	567,000
HCFC-141b	CH_3CFCl_2	500[h]	61,647
HCFC-142b	CH_3CF_2Cl	1000[h]	128,000
HFC-152a	CH_3CHF_2	1000[h]	383,000
HCFC-225ca	$CF_3CF_2CHCl_2$		31,000[j]
HCFC-225cb	CF_2ClCF_2CHFCl		31,000[j]
HFC-227ea	CF_3CHFCF_3		>800,000[k]
PFC-31-10	$CF_3CF_2CF_2CF_3$		>800,000[l]

[a] Refs. 7 and 27.
[b] Except for CO_2, no compound has a higher TLV than 1000 ppm.
[c] Approximate lethal concentration, inhalation by rats, 4 h exposure unless noted otherwise.
[d] 15 min exposure, mouse.
[e] 15 min exposure.
[f] 2 h exposure.
[g] Suspected carcinogen in humans.
[h] Du Pont Allowable Exposure Limit.
[i] 30 min exposure, mouse.
[j] Ref. 28.
[k] Unpublished results, Great Lakes Chemical Co.
[l] Unpublished results, 3M, Inc.

1,1,1-trichloroethane, and specify stepped-up timetables for total phaseout of ozone depleting chemicals by the year 2000.

In April of 1991, the U.S. National Aeronautics and Space Administration concluded that ozone depletion was occurring even faster than had been estimated, and at the third meeting of the parties to the Montreal Protocol in June of 1991, an earlier phaseout of controlled substances was proposed. An assessment of the technical and economic consequences of a 1997 phaseout is currently underway, and further acceleration of the phaseout schedule to as soon as 1995 seems likely. Many countries already have unilaterally banned or curbed the use of controlled substances well ahead of the Montreal Protocol timetable. As of early July 1992, there were 81 parties to the Protocol.

Table 8. Alternatives to CFCs

CFC	Application	Near-term substitute	Long-term substitute
CFC-11	blowing agents and refrigerants	HCFC-123 HCFC-22 HCFC-141b HCFC-142b	HFCs HFC-152a blends
CFC-12	refrigerants	HFC-134a HCFC-22	HFC-134a HFC-152a blends
CFC-113	cleaning agents	blends/azeotropes HCFC-225ca/cb	HFCs
CFC-114	blowing agents and refrigerants	HCFC-124 HCFC-142b blends/azeotropes	HFCs
CFC-115	refrigerants	HFC-125 blends/azeotropes	HFC-125
H-1301	fire extinguishant	HFC-23 HFC-125 PFC-31-10	HFC-23 HFC-227ea
H-1211	fire extinguishant	HCFC-123 HBFC-22B1 HBFC-124B1 PFC-51-14	HFCs

3. Chlorofluorocarbon Alternatives

3.1. Properties

The ideal substitute should have identical or better performance properties than the CFC it replaces. The ideal CFC substitute must not harm the ozone layer, and must have a short atmospheric lifetime to ensure a low greenhouse warming potential (GWP). It also must be nontoxic, nonflammable, thermally and chemically stable under normal use conditions, and manufacturable at a reasonable price. The chemical industry has found substitutes that match many but not all of these criteria.

The general strategy has been to incorporate at least one hydrogen atom in the proposed CFC substitute's structure which provides a means for its destruction via hydrogen atom abstraction by tropospheric hydroxyl radicals. The haloalkylradicals thus formed are then rapidly degraded to acids and CO_2, which are both removed from the atmosphere by natural processes. Since fluorine does not participate in the ozone destruction cycle, a substitute composed of only hydrogen, fluorine, and carbon would be ideal, but HFCs for every application have not yet been identified. In some applications, HCFCs and even PFCs have been suggested as transitional replacements to accelerate phaseout of the much more harmful CFCs. Trade-offs will likely be required in most applications, and the alternatives that have been identified for the various markets are listed in Table 8.

The physical and environmental properties of the leading commercial CFCs and their proposed substitutes are compared in Tables 9 and 10. The HCFCs have relatively small but non-zero ozone depletion potentials (ODP) and low global warming potentials (GWP). Recent results indicate even these values may be 15% too high (37). The HFCs have zero ODPs and low-to-moderate GWPs. Perfluorocarbons also have zero ODPs, but very large GWPs.

Table 9. Physical Property Comparisons of CFCs and Their HCFC or HFC Substitutes

	CFC	Substitutes				CFC	Substitutes	
Property	CFC-11	HCFC-123	HCFC-22	HCFC-141b	HCFC-142b	CFC-113	HCFC-225ca[a]	HCFC-225cb[a]
molecular weight	137.37	152.9	86.47	116.95	100.47	187.38	202.94	202.94
boiling point, °C	23.8	27.9	−40.7	32	−9.8	47.6	51.1	56.1
freezing point, °C	−111.1	−107	−157.4	−103.5	−130.8	−35.0	−94	−97
critical temperature, °C	198.0	185	96.0	210	137.1	214.2		
critical pressure, kPa[b]	4408	3789	4977	4641	4123	3415		
viscosity,[c] gas, mPa·s(=cP)	0.0105_{24}	0.0136_{60}	0.0122_{0}	0.0129_{60}	0.01099_{25}	0.0108_{49}		
viscosity,[c] liquid, mPa·s(=cP)	0.43_{20}	0.449_{25}		0.409_{25}	$0.453_{-20.9}$	$0.497_{48.9}$	0.58_{25}	0.60_{25}
surface tension,[c] mN/m(=dyn/cm)	18_{25}		8_{25}			17.3_{25}	15.8_{25}	16.7_{25}
heat capacity,[c] kJ/(kg·K)[d]								
liquid	0.870_{25}	1.0174_{25}	1.0962_{-40}	1.1556_{25}	1.2979_{25}	0.912_{25}		
vapor at 101.3 kPa[b]	0.565_{25}	0.7201_{25}		0.7913_{25}	0.8792_{25}	0.674_{60}		
latent heat of vaporization, kJ/kg[d]	180.3	174.17	233.84	223.15	223.15	146.73		
solubility in water at 101.3 kPa,[b] wt %	0.11_{25}	0.39	0.30	0.021	0.14	0.017		
atmospheric lifetime, years[e]	55	1.71	15.8	10.8	22	110	2.8	8.0
ozone depletion potential (ODP)[e]	1.00	0.02	0.055	0.11	0.065	1.07	0.025	0.033
global warming potential (GWP)[e]	1.00	0.02	0.39	0.14	0.44	1.80		

[a] Ref. 25.
[b] To convert kPa to atm, divide by 101.3.
[c] At the temperature (°C) indicated by subscripts.
[d] To convert J to cal, divide by 4.184.
[e] Ref. 36.

3.2. Manufacture

The manufacture of CFC alternatives is a far more complex challenge than production of the CFCs themselves (38). The very design feature which makes the alternatives tropospherically labile, the hydrogen atom substituent, also significantly complicates their manufacture because of potential by-product formation or catalyst inactivation. At least a dozen different routes to HFC-134a have been identified, but a simple, single-step process is very unlikely (39). A two-step process that has been commercialized first involves reaction of trichloroethylene with HF in the vapor or liquid phase to form HCFC-133a (40, 41), which is then separated and reacts again with HF to form HFC-134a.

$$CCl_2{=}CHCl + 3\ HF \longrightarrow CF_3CH_2Cl + 2\ HCl$$

$$CF_3CH_2Cl + \text{excess HF} \longrightarrow CF_3CH_2F + HCl$$

The HCFC-123 alternative to CFC-11 is made by the fluorination of tetrachloroethylene with either liquid or gaseous HF (41). Further reaction of HCFC-123 with HF provides the HCFC-124 and HFC-125 alternatives.

$$CCl_2{=}CCl_2 + 3\ HF \longrightarrow CF_3CHCl_2 + 2\ HCl$$

$$CF_3CHCl_2 \xrightarrow{HF} CF_3CHClF + CF_3CHF_2$$

Table 10. Environmental Property Comparisons of CFCs and Substitutes

	CFC	Substitute	CFC	Substitutes		CFC	Substitute
Property	CFC-12	HFC-134a	CFC-114	HCFC-124	HCFC-142b	CFC-115	HFC-125
viscosity,[a] gas, mPa·s(=cP)	$0.0117_{4.4}$	0.0152_{60}	0.0118_{25}	0.0138_{60}	0.01099_{25}	0.0125_{25}	0.015_{25}
viscosity,[a] liquid, mPa·s(=cP)	0.398	0.205_{25}	0.485_{0}	0.0314_{25}	$0.453_{-20.9}$	0.193_{25}	0.104_{25}
heat capacity,[a] kJ/(kg·K)[b]							
liquid	0.971_{25}	1.428_{25}	1.016_{25}	1.130_{25}	1.298_{25}	1.192_{25}	1.260_{25}
vapor at 101.3 kPa[c]	0.607_{25}	0.854_{25}	0.711_{25}	0.741_{25}	0.879_{25}	0.686_{25}	0.707_{25}
latent heat of vaporization, kJ/kg[b]	165.1	219.8	136.0	167.9	223.2	126.0	159.0
solubility in water[a] at 101.3 kPa,[c] wt %	0.028_{25}	0.15_{25}	0.013_{25}	1.71_{24}	0.14	0.006_{25}	0.09_{25}
atmospheric lifetime, years[d]	116	15.6	220	7.0	22.4	550	40.5
ozone depletion potential (ODP)[d]	1.00	0.00	0.8	0.022	0.065	0.52	0.00
global warming potential (GWP)[d]	2.90	0.29	4.1	0.11	0.44	6.1	0.86

[a] At the temperature (°C) indicated by subscripts.
[b] To convert J to cal, divide by 4.184.
[c] To convert kPa to atm, divide by 101.3
[d] Ref. 36.

The HCFC-225 isomers designed to replace CFC-113 are manufactured by Lewis acid promoted addition of HCFC-21 to tetrafluoroethylene (25, 42).

$$CHCl_2F + CF_2{=}CF_2 \xrightarrow{AlX_3} CF_3CF_2CHCl_2 + CClF_2CF_2CHClF$$

Since HFC-134a likely will be the single largest volume CFC alternative produced, many manufacturers around the world are in the process of or have plans to commercialize it, each under their own trade name. United States and foreign trademarks and manufacturers of CFC alternatives are listed in Table 11.

3.3. Economic Aspects

Manufacturing facilities for CFC alternatives are just now coming on line. The size of the markets for the alternatives is estimated to be quite large (several thousand t/yr), but it will not be as large as the prior markets for CFCs themselves. This is largely because of the higher cost of the alternatives, typically 3–5 times that of the incumbents. Low value-in-use applications which cannot support the cost of the alternatives will disappear or will switch to not-in-kind alternatives such as hydrocarbons for foam blowing.

3.4. Health and Safety Factors

The toxicity of CFC alternatives is the subject of intense study. Fifteen fluorocarbon producers have formed the Program for Alternative Fluorocarbon Toxicity testing (PAFT) to share the costs associated with determining safe operating and handling procedures for the proposed CFC alternatives. Long-term chronic toxicity studies are still underway and results to date generally look encouraging, although prolonged exposure to HCFC-123 produced benign tumors in rats (43). The approximate lethal concentrations (ALC) are shown in Table 7.

Table 11. Trademarks and Manufacturers of CFC Alternatives

Country and trademark	Manufacturer
France	
Forane	Elf Atochem
Belgium	
Solkane	Solvay
Germany	
Frigen	Farbwerke Hoechst
Fridohna	Hüls
Italy	
Algogrene	Montedison
Japan	
Asahiflon	Asahi Glass
Daiflon	Daikin Kogyo
Suva	Du Pont Mitsui Fluorochemicals
United Kingdom	
Klea	Imperial Chemical Industries
Isceon	Rhône-Poulenc
United States	
Genetron	AlliedSignal Corp.
Suva	Du Pont
FM	Great Lakes Chemical Co.
3M Brand	Minnesota Mining and Manufacturing Co.

Hydrofluorocarbons generally are less toxic than HCFCs, with the notable exception of HFC-152, CH_2FCH_2F, which apparently can be metabolically converted to monofluoroacetic acid and is therefore quite toxic (44).

4. Fluorocarbons Containing Other Halogens

4.1. Properties

The physical and chemical properties of bromo- and iodofluorocarbons are similar to those of the chlorofluorocarbons except for higher densities and generally decreased stability. The stability of these compounds decreases as the ratio of bromine or iodine to fluorine increases. The reactivity of carbon–halogen bonds toward exchange by fluorine or homolytic cleavage increases in the order C–Cl, C–Br, C–I. Iodofluorocarbons and most bromofluorocarbons readily lose iodine or bromine radicals under photolytic, thermal, or radical initiation to give the corresponding carbon-centered radical. The physical properties of several examples are shown in Tables 12 and 13.

4.2. Manufacture

Brominated fluoromethanes are prepared industrially by the halogen exchange of tetrabromomethane or by the bromination of CH_2F_2 or CHF_3 at elevated temperatures (3). Other bromo- or iodofluorocarbons can be prepared by halogenating suitable fluorocarbons, including fluoroolefins, or by halogen exchange of perfluoroiodocarbons (47).

$$CF_3CH_2Cl + Br_2 \xrightarrow{500^\circ C} CF_3CHBrCl$$

Table 12. Physical Properties of Aliphatic Hydrobromofluorocarbons (HBFCs) and Hydroiodofluorocarbons (HIFCs)[a]

B(I)FC number	Formula	CAS Registry Number	Molecular weight	Boiling point, °C	Melting point, °C	Liquid density, g/mL at °C	Refractive index, n_D at °C
11B1	$CBrCl_2F$	[353-58-2]	181.82	52	−106	1.9317_{20}	1.4304_{20}
11B2	CBr_2ClF	[353-55-9]	226.28	80		2.3172_{20}	1.4750_{20}
11B3	CBr_3F	[353-54-8]	270.74	106	−75	2.765_{20}	1.5256_{20}
12B1	$CBrClF_2$	[353-59-3]	165.37	−3.9	−161	1.850_{15}	
12B2	CBr_2F_2	[75-61-6]	209.83	24.5	−110	2.306_{15}	
13B1	$CBrF_3$	[75-63-8]	148.92	−57.8	−168	1.538_{25}	1.238^{25}
21B1	$CHBrClF$	[593-98-6]	147.38	−45	36.1	1.977_0	1.4144_{25}
21B2	$CHBr_2F$	[1868-53-7]	191.84	64.9	26.5	2.421_{20}	1.4685_{20}
22B1	$CHBrF_2$	[1511-62-2]	130.92	−15.5	−145	1.825_{20}	
113aB1	$CBrCl_2CF_3$	[354-50-7]	231.83	69.2		1.950_{20}	1.3977_{20}
114B2	$CBrF_2CBrF_2$	[124-73-2]	259.85	47.3	−110	2.163_{25}	1.367_{25}
115B1	$CBrF_2CF_3$	[354-55-2]	198.92	−21		1.810_0	$1.2966_{29.8}$
123B1	$CHBrClCF_3$	[151-67-7]	197.39	50.2		1.860_{20}	1.3700_{20}
123aB1a	$CHClFCBrF_2$	[354-06-3]	197.39	52.5		1.864_{25}	1.3685_{25}
124B1	CF_3CHFBr[b]	[124-72-1]	180.94	8.6	−80	1.85_{20}	
124aB1	CF_2BrCF_2H	[354-07-4]	180.94	10.8		1.900_{15}	1.321_{15}
132bB1a	$CH_2BrCClF_2$	[421-01-2]	179.40	68.4	−76	1.830_{20}	1.4018_{20}
133aB1	CF_3CH_2Br	[421-06-7]	162.94	26	−94	1.7881_{20}	1.3331_{20}
142B1	CH_2BrCHF_2	[359-07-9]	144.95	57.3	−75	$1.824_{18.5}$	$1.3940_{10.5}$
11I1	CCl_2FI	[420-48-4]	228.82	90.0	−107	2.313_{20}	1.510_{20}
13I1	CF_3I	[2314-97-8]	195.91	−22.5		2.361_{-32}	1.379_{-42}
21I2	$CHFI_2$	[1493-01-2]	285.83	100.3	−34.5	3.197_{22}	
22I1	CHF_2I	[1493-03-4]	177.92	21.6	−122	3.238_{-19}	
31I1	CH_2FI	[373-53-5]	159.93	53.4		2.366_{20}	1.491_{20}
113I1	$CClFICClF_2$	[354-61-0]	278.83	99		2.196_{25}	1.447_{25}
133aI1	CH_2ICF_3	[353-83-3]	209.94	55		2.142_{25}	1.3981_{25}

[a] Refs. 8 and 9.

[b] Ref. 45.

$$Cl_4 + IF_5 \longrightarrow CF_3I$$

$$CF_2{=}CF_2 + I_2 \longrightarrow ICF_2CF_2I$$

$$5\ CF_2{=}CF_2 + IF_5 + 2\ I_2 \longrightarrow 5\ CF_3CF_2I$$

$$CF_3\,(CF_2)_6\,CF_2I + Br_2 \xrightarrow{100-290^\circ C} CF_3\,(CF_2)_6\,CF_2Br$$

Table 13. Physical Properties of Telomer Iodides[a]

Formula	CAS Registry Number	Molecular weight	Boiling point, °C	Melting point, °C	Liquid density, g/mL at °C	Refractive index, n_D at °C
CF_3CF_2I	[354-64-3]	245.92	13		2.072_{28}	$1.3378_{0.5}$
$CF_3(CF_2)_3I$	[423-39-2]	345.91	67		2.0424_{25}	1.3258_{25}
$CF_3(CF_2)_5I$	[355-43-1]	445.92	118	−46	$2.028_{26.4}$	1.3220_{20}
$CF_3(CF_2)_7I$	[507-63-1]	545.96	163	20.8	2.008_{25}	
$CF_3(CF_2)_9I$	[423-62-1]	645.98	195	65.5	1.9400_{70}	$1.3350_{25.5}$
$CF_3(CF_2)_2I$	[754-34-7]	295.93	41.2	−95.0	2.0026_{20}	1.3281_{20}
$CF_3(CF_2)_4I$	[638-79-9]	395.94	94.4	−50.0	$2.0349_{27.8}$	$1.3389_{0.5}$
$CF_3(CF_2)_6I$	[335-58-0]	495.96	137.5			1.3230_{30}
$CF_3(CF_2)_8I$	[558-97-4]	595.97	181			
$I(CF_2)_2I$	[354-65-4]	353.82	112		2.629_{25}	1.4895_{25}
$I(CF_2)_4I$	[375-50-8]	453.82	150	−9.0	2.4739_{27}	$1.4273_{26.2}$

[a] Refs. 9 and 46.

The higher molecular weight perfluoroalkyl iodides are prepared by telomerization of tetrafluoroethylene with lower molecular weight perfluoroalkyl iodides (46, 48).

$$CF_3CF_2I + m\,CF_2{=}CF_2 \xrightarrow{\text{cat. }SbF_3/IF_5} CF_3CF_2\,(CF_2CF_2)_m\,I$$

$$ICF_2CF_2I + n\,CF_2{=}CF_2 + \text{heat} \longrightarrow ICF_2CF_2\,(CF_2CF_2)_n\,I$$

4.3. Health and Safety Factors

Fluorocarbons containing bromine or iodine are more toxic than the corresponding chloro compounds. When the ratio of the fluorine to other halogens is high, the toxicity can be quite low, especially for bromofluorocarbons. Perfluoro-1-bromooctane [423-55-2] has an LD_{50} of greater than 64 mL/kg when administered into the gastrointestinal tract, and has little effect when instilled into the lungs (49). Other examples are included in Table 7.

4.4. Uses

The most important industrial products of this class have been the fire-extinguishing agents $CBrClF_2$ and $CBrF_3$. The latter is considerably more effective than CO_2, and is nontoxic as well as its decomposition products (50). It is used in commercial aircraft for in-flight engine fires and in portable fire extinguishers for both military and civilian markets. Both of these Halons have very high ozone depletion potentials, and their production is scheduled to be completely phased out by the year 1994 (51). Suitable replacements are being sought, and the properties of some leading candidates are compared in Table 14.

Halothane, $CF_3CHClBr$, was a widely used anesthetic which has the advantages of nonflammability, high anesthetizing power, and general lack of postnarcotic effects, but it has lost its leading market share to the fluorinated ethers enflurane, $CHClFCF_2OCHF_2$, and isofluorane, $CF_3CHClOCHF_2$ (52, 53) (see ANESTHETICS).

Perfluorooctyl bromide [423-55-2], which has one of the highest oxygen-dissolving capabilities among fluorinated liquids and is readily emulsified, shows great promise in various medical applications such as tissue oxygenation, chemotherapy, and radiographic imaging (20, 21, 49).

The use of α,ω-diiodoperfluoroalkanes as chain-transfer agents in the manufacture of fluoroelastomers (54) is the only direct commercial application of iodofluorocarbons, although several telomer iodides, such as

Table 14. Physical Property Comparisons of BFCs and Their Substitutes

	BFC	Substitutes			BFC	Substitutes		
Property	H-1301	HFC-23	HFC-227ea	PFC-31-10	H-1211	HCFC-123	HBFC-22B1	PFC-51-14
molecular weight	148.91	70.01	170.03	238.03	165.4	152.9	130.92	338.0
boiling point, °C	−57.8	−82.0	−16.4	−2.0	−4	27.9	−15.5	56
freezing point, °C	−168.0	−155.2	−131	−128.2	−160.5	−107	−145	−90
critical temperature, °C	67.0	25.7	101.7	113.2	153.8	185	138.8	178.0
critical pressure, kPa[a]	3964	4810	2909	2323	4104	3789	5129	1835
critical density, kg/cm^3	745	525	621	630	713			
viscosity,[b] gas, mPa·s	0.0016_{25}	0.0144_{25}	0.0132_{25}		0.0138_{25}	0.0136_{60}	0.0153_{25}	
viscosity,[b] liquid, mPa·s	0.32_{40}	0.368_{80}	0.184_{25}	0.607_{25}	0.292_{25}	0.449_{25}	0.269_{25}	0.700_{25}
heat capacity, kJ/(kg·K)[c]								
liquid	0.828_{0}	1.211_{-100}	1.102_{25}	1.045_{25}	0.742_{25}	1.017	0.814_{25}	
vapor at 101.3 kPa[d]	0.474_{25}	0.736_{25}	0.777_{25}	0.805_{25}	0.474_{25}	0.720	0.478_{25}	
latent heat of vaporization, kJ/kg[c]	118.7	251.2_{-100}	132.7	96.3	149.35	174.17	172.08	88.4
relative dielectric strength, $N_2 = 1$	1.83	1.04		5.25				
solubility in water[b] at 101.3 kPa, wt %	0.03_{25}	0.10_{25}		0.001_{25}		0.39_{25}		0.001_{25}
atmospheric lifetime, years[e]	67	310[f]		>500	19	1.71	5.6	>500
ozone depletion potential (ODP)[e]	16.0	0.00	0.00	0.00	4.0	0.02	1.40	0.00
global warming potential (GWP)[e]	1.6	8		>8		0.02		>8

[a] To convert kPa to atm, divide by 101.3.

[b] At the temperature (°C) indicated by subscripts.

[c] To convert J to cal, divide by 4.184.

[d] 101.3 kPa = 1 atm·

[e] Ref. 36.

[f] Estimated value.

$CF_3(CF_2)_7I$ [507-63-1] and $CF_3(CF_2)_7CH_2CH_2I$ [2043-53-0], are intermediates in the manufacture of oil and water repellants, surfactants, and fire-extinguishing foams (55). The alcohols derived from perfluoroalkane carboxylic acids, eg, $CF_3(CF_2)_nCH_2OH$, or from the telomer iodides, eg, $CF_3(CF_2)_nCH_2CH_2OH$, are used to prepare fluorinated acrylate esters. Aqueous dispersions of the fluoroacrylate polymers are used as soil, water, and oil repellents for fabrics (56) (see Waterproofing). They are sold under the Scotchgard (3M) and Zepel or Zonyl(Du Pont) trade names.

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