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Source Book of INDUSTRIAL SOLVENTS

VOLUME II

Halogenated Hydrocarbons

By

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PUBLISHER'S PREFACE

The first volume of this series was entitled "Handbook of Solvents." Since its publication it has become apparent that some modification of this title was necessary in view of the probability of confusion with other books in the field. Consequently it was decided to retitl e the series "Source Book of Industrial Solvents." Volume I is subtitled "Pure Hydrocarbons," and Volume II, which now appears under the new title, is subtitled "Halogenated Hydrocarbons."

Admittedly this is a somewhat awkward change in the middle of the stream, but the publishers felt that this statement of the situation would be sufficient to clarify the matter in the minds of the users of these books.

This volume carries out the basic idea of presenting important physical property data on a chemically related group of industrial solvents, together with sufficient background of textual material to provide a useful reference book.

It is planned to continue this series of volumes covering additional important groups of industrial solvents so that eventually the series will in fact constitute a valuable compendium of data on this rapidly expanding field of materials.

Reinhold Publishing Corporation

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Section I
HALOGENS

HALOGENS

The halogens are a remarkable family of elements, marked by their great chemical activity and the unique properties which have served as valuable instruments in advancing chemical science and in adding a new and unprecedented scope to the solvent field. Stability, nonflammability, and a wide range of solvency are but a few of the characteristics imparted by their application.

In the stirring times of rapid chemical development during the nineteenth century, the use of halogens in advancing chemical theory has been the forerunner of the diversity in hydrocarbon uses and products which have distinguished the twentieth century for its multiplicity of industrial output. The presentations of both Laurent, in 1837, and Dumas, in 1839, of the new principle of substitution in a hydrocarbon by which the electropositive halogen replaces the electropositive hydrogen in the molecule, thereby producing modifications and additions in the properties of the derivative, have given stimulus to and influenced the direction of chemical research.

The term "halogen" is applied to five elements—fluorine, chlorine, bromine, iodine, and the recently discovered astatine. Berzelius named them halogens from the Greek word meaning "salt-producer" because of the similarity of their sodium salts to the salt of the sea. These elements and their compounds resemble each other in their general chemical behavior while, in relation to their atomic weights, they show a gradual transition in their physical properties. Thus, as the atomic weight increases, fluorine and chlorine occur as gases, bromine as a liquid, and iodine as a solid, fluorine being the lightest and iodine the heaviest halogen, except for the rare astatine.

The halogens appear in Group VII, subgroup B, of the Periodic Table and their atoms, having seven valence electrons, combine readily with one electron

to form a stable negative ion having a completed octet with a charge of minus one. In their elemental state, they exist as diatomic molecules. Fluorine has the highest electron affinity and is therefore the most reactive of the halogens; it forms fluorides with evolution of considerable energy. Iodine is the least reactive of the halogens. Free fluorine is prepared with great difficulty, while free iodine is the easiest to prepare. The relative reactivity decreases from fluorine to iodine. Thus, the halogen of lower atomic weight displaces one of higher atomic weight. As halide ions, the relative activity of the halogens in the oxidized state is the reverse of the reduced state. For example, chlorine will reduce elemental iodine dissolved in an aqueous solution of potassium iodide, while iodine will displace chlorine in potassium chlorate forming the more stable potassium iodate. Thus, iodine as the iodide is the best reducing agent in the halogen family, and chlorine as the chlorate is the best oxidizing agent. Except for fluorine, the halogens are readily oxidized in an alkaline medium.

In addition, the color of the halogens is found to deepen from fluorine to iodine, the boiling points and density increase, and the average of the properties of chlorine and iodine approximate the properties of bromine. They form salts by direct union with metals. The binary compounds of halogens, excluding the oxides, are known as "halides" and solutions of metal halides, except for some fluorides, are soluble in water.

The halogens unite with hydrogen, but their affinity for hydrogen decreases as their atomic weight increases. Thus, fluorine unites explosively at very low temperatures and in the dark; iodine and hydrogen unite with difficulty and decompose readily upon heating. There is a marked difference in water solubility between fluorine and the other three members of the group. Sodium chloride, sodium bromide, and sodium iodide are readily soluble in water, but sodium fluoride is only slightly soluble. On the other hand, silver chloride, silver bromide, and silver iodide are

practically insoluble in water, but silver fluoride is appreciably soluble in water. Also, fluorine has a tendency to form double salts which does not occur with other halogens. The halogens are oxidizing agents but the heavier the halogen, the weaker is its oxidizing power.

Halogenation refers to the process of introducing one or more halogen atoms into an organic compound either by photochemical or thermal means. The photochemical halogenation of hydrocarbons has occupied the attention of chemists for over 100 years following Dumas' discovery, in 1840, of the photochemical chlorination of methane. Photochemical reactions are those initiated or otherwise influenced by the absorption of light. In mixtures of hydrogen and chlorine, the light initiates the reaction which then runs to completion.

Except for iodine, the halogens react readily with paraffin hydrocarbons. Their halogenation is accomplished either with light or heat, by substitution of one or more hydrogen atoms with halogen atoms. The halogenation of unsaturated paraffins is accomplished either in the presence of light or in the dark, either in liquid or vapor phase, either with or without a catalyst, and either by addition or substitution, the method being determined by the temperature used.

Generally, aliphatic halogenations are carried out in the presence of organic peroxides or a small amount of oxygen in the reaction system, or by the use of light, with a relatively low initial halogen concentration which is constantly renewed as the halogen is expended.

Aromatic halogenations by substitution require relatively high initial halogen concentrations and the reaction is catalyzed by metallic halides such as ferric chloride or ferric bromide.

Most unsaturated aliphatic compounds will halogenate by addition with bromine, chlorine, hydrogen chloride, hydrogen bromide, or hydrogen iodide in the presence of concentrated sulfuric acid, and at ordinary temperatures.

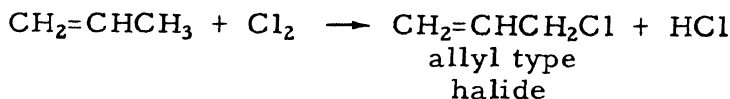
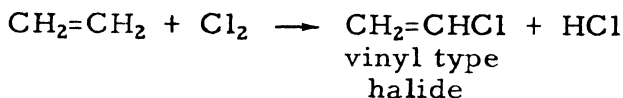
When olefins are chlorinated by addition, saturated compounds result in which two chlorine atoms are attached to adjacent carbon atoms, thus:



The addition reaction gives essentially one product. When a similar process is carried out with bromine below 100°C, dibromides result and the bromine atoms are likewise attached to adjacent carbon atoms:



When olefins are halogenated by substitution, vinyl or allyl type haloolefins result:



The vinyl halides are characterized by their unreactivity; the allylic halides are very reactive and are therefore largely used in synthesis rather than as solvents.

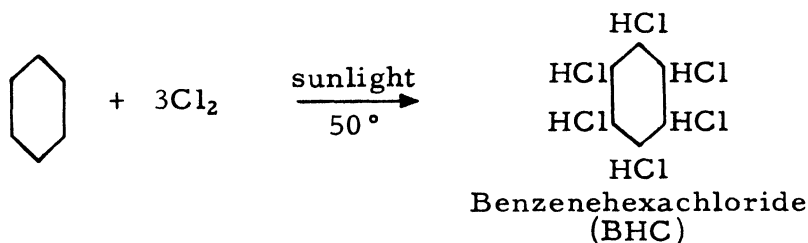
The straight-chain olefins were first chlorinated by substitution in 1936. This was found to be possible at temperatures ranging from 400 to 600°C when chlorine was in a 1:7 mixture with the olefin. Under such conditions, ethylene yields vinyl chloride and propylene yields allyl chloride.

Other methods for synthesizing vinyl or allyl halides are by the addition of a hydrogen halide to an acetylene or by dehydrohalogenation of polyhalo compounds:



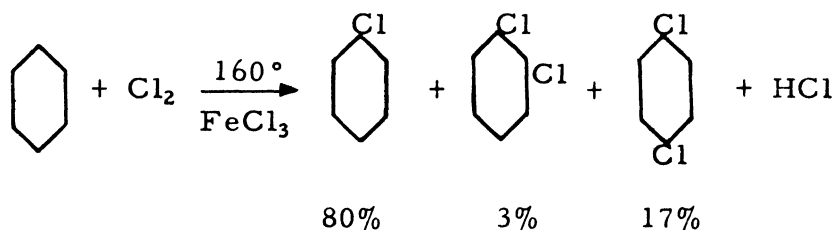
The halogenation of unsaturated paraffins gives products which find application as valuable unreactive chlorinated solvents and extractants, vapor degreasants, soil fumigants, anesthetics, dehydrating agents; they are also used in the manufacture of resins and in the synthesis of other organic compounds.

The halogenation of aromatic hydrocarbons is accomplished by either addition or substitution. The addition process involves the treatment of an aromatic compound such as benzene with chlorine or bromine in either sunlight or by the use of other actinic light, yielding a hexahalocyclohexane:



Halogenation by this process is possible only with complete absence of any of the common halogen carriers.

The substitution process for halogenating benzene and its homologs is carried out in the dark with catalytic agents, yielding the following halobenzenes:



ASTATINE

Astatine, At, the fifth halogen, was first detected by Allison and Murphy in 1931 by means of magneto-optic measurements and was given the name "alabamine." Its actual discovery, in 1940, was credited to Corson, MacKensie, and Segre and it was named "astatine" from the Greek word meaning "unstable" because of the short half-life of the isotopes of this radioactive element. Astatine is produced by β -disintegration of radium A and thorium A. It is the heaviest of the halogens. Its atomic number is 85 and its atomic weight is 211.

TABLE I
Halogens

Properties	Fluorine	Chlorine	Bromine	Iodine	Astatine
Atomic weight	19	35.46	79.92	126.92	210
Symbol	F	Cl	Br	I	At
Physical appearance	Gas	Gas	Liquid	Solid	
Color of gas	Pale yellow	Greenish	Brownish	Violet	
Melting point, °C	-223°	-102°	-7.3°	113°	
Boiling point, °C	-187°	-34.6°	58.8°	184.35°	
Specific gravity	1.08 (liq.)	1.55 (liq.)	3.19 (liq.)	4.93 (solid)	
Atomic volume*	16.7	22.9	25.1	25.7	
Atomic number	9	17	35	53	85

*Atomic volume = $\frac{\text{Atomic weight}}{\text{Specific gravity}}$

Section II

FLUORINATED HYDROCARBONS

FLUORINE

Fluorine, the most active of the nonmetallic elements, is a unique element. Until about two decades ago, it was treated with a wariness that mirrored the respect which its violent nature demanded, before methods were devised for dealing with its disruptive and explosive reactions. The urgent need of chemicals with unique characteristics for the development of superior mechanisms of war focused attention on fluorine and fluorine compounds in 1941. The description of fluorocarbon properties made by Simons and Black, in 1939, attracted the attention of the navy which was searching for possible nonexplosive, non-flammable liquids for its hydraulic gun-aiming systems on naval vessels. The Atomic Energy Program was also looking for materials that could be applied as sealants, coolants, and lubricants for handling certain corrosive substances used in the separation of uranium isotopes. After tests made on the available fluorocarbons proved satisfactory for these purposes, the Manhattan Project was initiated early in 1942. This fluorine research project produced staggering results. The concerted effort of universities and industrial laboratories under this program brought into existence a large number of fluorocarbons as well as an accumulation of data on their properties.

The possibilities of this new field of chemistry kindled the imagination and enthusiastic enterprise of both academic fields and industry alike. However, before the fluorocarbons could attain commercial importance, it was necessary to "tame" the fluorine element essential for their production. By acquiring technical means of generating fluorine on an industrial scale and employing methods for successfully compressing, bottling, storing, and then neutralizing and disposing of the toxic products and by-products resulting from industrial fluorination, the phenomenally inert fluorinated hydrocarbons were finally brought out of the academic field. Before World War II, elemental fluorine sold for \$75 a pound. Today, the price is

expected to be reduced to twenty five cents a pound. By means of the liquefaction-pressure distillation method, fluorine can be compressed into nickel and steel cylinders at 400 psi. It has been established that fluorine can be safely shipped by common carrier in nickel or steel cylinders containing 5 pounds of gas at 400 psi. The low critical temperature of fluorine, -129°C , and its corrosive properties add considerably to the hazards and expense of transportation. Field studies have been made to determine the possibilities of handling fluorine at 1500 to 2000 psi. Under such conditions, the pressure should be remotely controlled through protective barriers.

Fluorine, the most electronegative element, having a potential of -2.84 volts, is heavier than air but the lightest of the halogens. It is located in the Periodic Table as the first member of Group VII-B, and is univalent. Because of its extreme activity, it is never found in an uncombined state; it is widely distributed in rocks, mostly of an acidic nature. Chief among these is fluorite, or fluorspar, as it is known in Great Britian, a mineral composed mainly of calcium fluoride. Fluorine is also contained in some phosphates such as fluorapatite and phosphorite, and in some silicates such as topaz and tourmaline.

Compared with chlorine, fluorine is only half as abundant, but it is about equal to the world supply of nitrogen or oxygen. Fluorine is a greenish-yellow gas with a sharp and irritating odor. Dilute solutions are colorless but more concentrated solutions have a greenish cast.

Although fluorine is the most reactive element known, its activity can be modified by controlling the temperature. It will not act upon glass and some metals at low temperatures, but at elevated temperatures it will burn. In a dry state it will not react with hydrogen. Under suitable conditions, fluorine combines readily with practically all substances and most materials will react with it at room temperature.

Carbon tetrafluoride is the only organic substance which is completely resistant to fluorine. The inert gases and metal fluorides in their highest valence state are resistant to fluorine, but most inorganic substances will react with it. Metals which show excellent resistance to fluorine are nickel, monel, aluminum, and magnesium. The extent of its reactivity with metals is determined by the amount of fluorine, temperature, concentration, and time. Fluorine forms a stable compound with some metals in an initial layer that is adherent and invisible. This film prevents further action with fluorine, thus explaining the resistance shown by nickel and monel to this element. Fluorine is highly corrosive at either high or low temperatures.

The mineral fluorspar was first mentioned as a fluxing material by Basil Valentine who lived in the fifteenth century and in 1529 it received attention in the "Bermannus" of Georg Agricola, a Leipzig metallurgist. Interest in fluorine compounds increased with the recognition of the corrosion of glass by fluorspar and an acid. H. Schwankardt, in 1670, succeeded in etching glass by the action of fluorspar and sulfuric acid. M. Pauli, in 1725, mixed nitric acid and powdered fluorspar to make a liquid for etching glass. But interest in fluorine compounds received its major stimulus when the isolation of hydrogen fluoride was accomplished by Scheele in 1771 and again by Gay-Lussac and Thenard in 1809. Davy and Ampere recognized it in 1813 but were unable to isolate it. After years of persistent effort, Henri Moissan succeeded in preparing and isolating fluorine for the first time on June 26, 1886, thereby marking a day of immeasurable importance in the history of chemistry.

Moissan succeeded in isolating fluorine by the electrolysis of anhydrous hydrogen fluoride in the presence of potassium hydrogen fluoride which acted as a conductor of the electric current. Similar methods are employed today but they have been much improved with the development of better cells, electrodes, and electrolytes.

After fluorine was recognized as an element, frequent attempts were made to obtain it from its compounds. However, because of its violent activity, progress of fluorine chemistry was impeded. Special techniques were required for handling it safely and only the more courageous were willing to risk further study. Among these were Moissan and others in France, Ruff and associates in Germany, and Swarts of Belgium. Chemists in the United States took a more active interest in fluorine research shortly after 1920, bringing to light the unusual properties of the fluorine compounds developed.

Although fluorine chemistry is a newcomer to chemical science, many of the inorganic fluorides have been of commercial importance for some time. Among these are fluorite, used in general metallurgy; cryolite, familiar in the metallurgy of aluminum; and others such as sodium fluoride and barium fluosilicate long used as insecticides. Hydrogen fluoride is by far the most important of the inorganic fluorides. As an alkylation catalyst, it is used extensively by the petroleum industry in low-temperature alkylation of paraffin hydrocarbons. The high-octane gasoline produced by this method contributed to the air supremacy held by the Allies during World War II. Hydrogen fluoride is highly regarded as an ionizing solvent; it has a relatively high density and high dielectric constant. Its boiling point is relatively high for its molecular weight.

Bromine fluoride and chlorine fluoride are very reactive and have been used by the Germans for incendiary purposes. Sodium fluoride is well known as an insecticide and disinfectant. Fluorides produce many complex salts with alkaline-earth fluorides. Because fluorides tend to form double salts, large numbers of inorganic fluorine compounds can be made. Boron trifluoride is used extensively as a catalyst of the Friedel-Crafts type. It is used as a catalyst in the preparation of esters derived from alcohols, aliphatic or aromatic acids, olefins and acids, nitriles and alcohols, etc. A more recent development in the

chemistry of fluorine has been a class of compounds known as "fluorocarbons."

Moissan observed that fluorine reacted with many organic compounds with such explosive force that the molecule was decomposed, forming carbon tetrafluoride, with hydrogen fluoride and carbon as decomposition products. Other investigators continued to lay the foundation for the later structure of organic fluorine chemistry. Swarts, in Belgium, developed several methods for preparing fluorine compounds, which ultimately led to the industrial use of aliphatic polyfluorohalo compounds as refrigerants, following the adaptation of these methods by Midgely and Henne about 1930. Essentially, the method is based on the reaction of a mixture of a polychloro compound with anhydrous hydrofluoride, using antimony trifluoride as a catalyst.

Other methods to control the interaction of fluorine and organic substances continued to be developed with the outcome that in the short period of fluorocarbon development, over a thousand such compounds have been prepared and identified.

The fluorocarbons are regarded as the parent compounds of a separate branch of chemistry, similar to the position held by hydrocarbons in relation to organic chemistry. The behavior of the fluorocarbons appears to substantiate the prediction that the many varieties of skeleton structures present in hydrocarbons can be duplicated by the fluorocarbons.

From a study of this class of compounds, basic facts of behavior have been revealed. A fluorocarbon molecule containing a single fluorine atom will be unstable, as witnessed in the ready loss of hydrogen fluoride from C_5 upwards in the monofluoroparaffins.

Compounds containing a single fluorine atom will be more stable with the addition of another halogen atom on the same carbon atom. An example of this is CH_2ClF which is more stable than CH_2Cl_2 , but less stable than CH_2F_2 .

The C-F bonds will be considerably strengthened when two or more fluorine atoms are attached to one carbon, and such a molecule stabilizes a third halogen when attached to the same carbon atom. This behavior, however, causes difficulty in the third stage of fluorination. The presence of two fluorine atoms on one carbon atom also stabilizes a halogen attached to an adjacent C atom.

Fluorocarbons containing more than one fluorine atom have been placed in a class of their own and named "fluorochemicals," on the assumption that the properties of these polyfluorides are sufficiently different from monofluorides to justify such a distinction. Fluorochemicals have been defined as organic compounds in which a large percentage of the hydrogen atoms directly attached to the carbon has been replaced by fluorine. These polyfluorides have received commercial importance, examples of which are perfluoropropane (C_3F_8), diperfluorobutyl ether ($C_4F_9OC_4F_9$), and trifluoroacetic acid (CF_3CO_2H).

Table 2 gives the average values of the heat of formation (ΔH_f) of gases of fluorocompounds (1).

TABLE 2

Fluoro-compound	ΔH_f , kcal/mole	Related compounds	ΔH_f , kcal/mole	
			A	B
CF_4	$-218 \pm 2^*$	CH_4	-17.89	
CF_3Cl	-171 ± 1	CH_3Cl	-19.58	
CF_2Cl_2	-112 ± 2	CH_2Cl_2	-21	-22.3
$CFCI_3$	-70 ± 4	$CHCl_3$	-24	-25.0
		CCl_4	-25.5	-22.2
C_2F_6	-303 ± 2	C_2H_6	-20.24	
$(CF_2Cl)_2$	-213 ± 3	$(CH_2Cl)_2$	-32	-30.3
		C_2Cl_6	-34	-35.4
C_2F_4	-162 ± 1	C_2H_4	+12.5	
CF_2CFCI	-126 ± 2	CH_2CHCl	+7.5	
		C_2Cl_4	+6	-3.6

* Cf. von Wartenberg's value, -231 ± 3 kcal/mole $\equiv$ -229 kcal/mole when corrected to graphite.

The fluorocarbons as a new phase of chemistry have given birth to the terms forming the basis of a nomenclature specific to this group of compounds. Some of these have already become part of the descriptive language of fluorocarbons while others are still in question. The prefix "perfluoro" before an organic compound indicates that all the hydrogen atoms have been replaced by fluorine. Perfluoromethane (CF_4) and perfluorocyclopentane (C_5F_{10}) are examples of such compounds. Simons has introduced a system of nomenclature in which the term "for" is placed before the final syllable of the name of an organic compound to distinguish the fluorocarbons. Examples of these are CF_4 named methforane, C_2F_4 , ethforene, and C_6F_6 , benzforene.

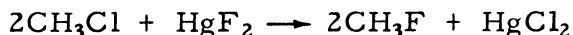
The nomenclature, spelling, and pronunciation of halogenated derivatives of hydrocarbons, the use of "per" in many halogenated organic compounds, and the use of "H" to designate the position of hydrogens in almost completely fluorinated organic compounds are given in a report of the American Chemical Society, published in Chemical and Engineering News, Vol. 30, pages 4513, 4514 and 4515, October 27, 1952.

The exceptional properties of the fluorocarbons have been the prime factor leading to their exploration and development. The saturated hydrocarbons exhibit a remarkable chemical and thermal stability approaching that of the inert gases. They will resist chemical action up to about 500°C , and their resistance to combustion is so great that not only are they difficult to set on fire, but they will smother a fire already started. They are stable to acids, alkalis, and oxidizing agents but are attacked by elemental fluorine, and by metallic sodium and potassium at elevated temperatures (400°C and above). The fluorocarbons are very transparent and have low indices of refraction, high fluidities, low surface tensions, and high densities. Their boiling points are relatively low compared with compounds having similar molecular weights. They have high electrical resistance, low dielectric loss factor, and zero water absorption.

They are miscible with one another in all proportions, slightly soluble in nonpolar solvents, and insoluble in polar solvents. They form azeotropes with themselves and other liquids.

The slow progress in the development of fluorine chemistry was largely due to the violent reaction of fluorine. Although fluorine reacts directly with hydrocarbons to form fluorides, the reaction is far too violent for personal safety. Some reactions have been carried out by carefully controlling both the fluorine concentration and temperature, but the splitting of C-C bonds is not eliminated. Although the bonds of the atoms in a fluorine molecule are stronger than those of other halogens, once they are released they combine more easily with hydrogen and hydrocarbons than halogens with a higher molecular weight. The reaction liberates intensive heat and the new bonds formed are extremely strong. Such violent reaction has necessitated the search for indirect methods of preparing fluorine compounds.

A number of methods have been devised for introducing fluorine in an organic molecule. A replacement method in which chlorine, bromine, or iodine is replaced by fluorine in organic halides or polyhalides, employing inorganic fluorides has been found of value.



Other methods that have been devised are as follows:

A method involving the controlled interaction of fluorine and organic compounds.

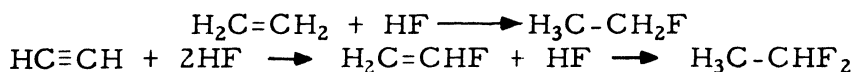
An electrochemical process in which solutions of organic compounds in anhydrous hydrogen fluoride are subjected to electrolysis under controls that prevent the production of free fluorine. This process, invented by Simons, is unique in that the product is obtained in practically one step.

A method based on the use of such inorganic high fluorides as cobalt trifluoride or silver difluoride to carry out the replacement of hydrogen by fluorine in

organic compounds is found to be superior in producing fluorocarbons of moderate molecular weight such as C_6F_{12} , C_7F_{16} , and C_8F_{16} .

Some examples of fluorination in which cobalt fluoride (CoF_3) is used are given by Fowler and Weber (2, 4). See Tables 3 and 4.

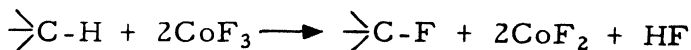
A method in which fluorination is carried out by adding hydrogen fluoride to olefins or acetylenes, producing stable polyfluorides known commercially as "Genetrons" and "Freons."



A method known as the Balz-Schiemann reaction in which fluorine is introduced by the decomposition of diazonium fluoroborates.

Among the methods of limited interest is one based on the decomposition of quaternary ammonium fluorides and another based on the conversion of alcohols to fluorides.

The saturated hydrocarbons such as the fluoroparaffins and the fluoronaphthenes can be prepared by the following fluorination methods using elemental fluorine. In one, the hydrocarbon is vaporized, diluted with nitrogen and passed over a bed of CoF_3 at 200 to 350°C. The element fluorine is passed over at 200 to 250°C. MnF_3 , CeF_4 and AgF_2 will behave in a similar manner to CoF_3 .



Another is a continuous one-step catalytic process. The vaporized hydrocarbon and fluorine gas are diluted with nitrogen and mixed gradually at a temperature of 150 to 325°C. This is carried out over a catalyst of fine copper turnings or ribbon, covered with a thin layer of Ag fluorides.

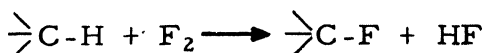


TABLE 3
Reaction of Hydrocarbons with CoF_3 (4)

Starting Material	Pure Product	Crude Yield, %	Yield of Pure Product, %	
			Single Pass	Repass
Bis(trifluoromethyl)benzene (mixture of 1, 3- and 1, 4-)	Perfluorodimethylcyclohexane	97 ¹	83 ¹	88 ¹
n-Heptane	Perfluoro-n-heptane	91 ¹	68 ¹	70 ¹
XCT white oil		70 ^{1, 2}	..	..
Diol 45		51 ^{1, 2}	..	..
n-Butane	Perfluoro-n-butane	45 ³	..	..
n-Pentane	Perfluoro-n-pentane	67	58	..
Cyclopentane	Perfluorocyclopentane	46 ³	28	..
Dimethylcyclopentane	Perfluorodimethylcyclopentane	83	38	..
Ethylcyclopentane	Perfluoroethylcyclopentane	68	59	..
Benzotrifluoride	Perfluoromethylcyclohexane	88	77	..
o-Xylene	Perfluoro-o-dimethylcyclohexane	63	42	..
m-Xylene	Perfluoro-m-dimethylcyclohexane	66	50	..
p-Xylene	Perfluoro-p-dimethylcyclohexane	55	42	..
Mesitylene	Perfluoro-1, 3, 5-trimethylcyclohexane	54	27	..
Indan	Perfluorohexahydroindan	43	20	..
Cetane	Perfluorocetane	40	29	..
Diphenyl oxide	Perfluorodicyclohexylether	32	15	..

¹ Averages of many runs under optimum conditions.

² Based on conversion of $-\text{CH}_2-$ to $-\text{CF}_2-$.

³ Large handling losses.

⁴ Not distilled here.

TABLE 4
Preparation of Low Polymer Chlorotrifluoroethylene and Fluorination by Cobalt Trifluoride Treatment (3)

Run No.	Polymerization Conditions (Deviation from Standard)	Polymer Yield, % of CF_3CFCl Charged	Polymer of B.P. ¹ 120-220°C ¹ at 0.3 mm., wt % ²	Polymer of B.P. >220°C at 0.3 mm., wt % ²	CoF_3 Required, g CoF_3 /100 g Oil	Polymer Oil of B.P. 100-200°C at 0.3 mm., wt % ^{1, 2}
1	Standard conditions	86	26	51	97	27
2	CCl_2CCl_2 as solvent	66	16	74	..	..
3	CCl_4 as solvent	71	<10	>80	..	..
4	CHClCCl_2 added equimolar to CF_2CFCl	60	24	7	..	..
5	$\text{GF}_2\text{CFCl}/\text{CHCl}_3$ ratio, 1/18	76	33	39	99	26
6	$(\text{C}_6\text{H}_5\text{COO})_2/\text{CF}_2\text{CFCl}$ ratio, 1/10	94	37	49	98	27
7	$\text{C}_2\text{H}_5\text{OH}$ added, 1g/100 g CHCl_3	27	..	..	..	..
8	CHCl_3 used was U.S.P. grade	52	..	..	..	..
9	Extra care to remove oxygen	86	28	61	95	16 ³
10	Oxygen added, 50 lb/sq in gage	26	..	..	..	..
11	$(\text{CH}_3\text{COO})_2$ promoter; $(\text{CH}_3\text{COO})_2/\text{CF}_2\text{CFCl}$ ratio, 1/20	82	29	52	63	25
12	$(\text{CH}_3\text{COO})_2/\text{CF}_2\text{CFCl}$ ratio, 1/10	85	41	40	76	29
13	$(\text{CH}_2\text{ClCOO})_2$ promoter; $(\text{CH}_2\text{ClCOO})_2/\text{CF}_2\text{CFCl}$ ratio, 1/20	48	20	54	63	18 ³
14	$(\text{CH}_2\text{ClCOO})_2/\text{CF}_2\text{CFCl}$ ratio, 1/10	49	39	48	52	33

¹ Comparable data were available for 120-220°C b.p. fractions in all cases. The stabilized yields were obtained from a crude oil fraction of b.p. 110-240°C at 0.3 mm.

² Yields calculated on the basis of reacted CF_2CClF .

³ Large manipulative loss.

TABLE 5
The Rectification of Fluorinated Trichloroethylene at Various Molar Reaction Ratios and Temperatures (6)

Compound	B. P., °C	% Yield ¹ at Molar Reacn. Ratio and Reacn. Zone Temp. of				Prob. CF ₄ + CF ₃ Cl
		1:1:6 (71°)	1:1:15 (45°)	1:1:15 (120°)		
.....	<-78	1	} 1		} 2	
CF ₃ CF ₂ Cl + CF ₂ Cl ₂	-78 to +3	1	} 1			
C ₂ F ₄ Cl ₂	3-4	2				
C ₂ HF ₃ Cl ₂	27-30	4	4	3	CHFC1-CF ₂ Cl and/or CHF ₂ -CFCl ₂	
CF ₂ ClCFCl ₂	45-48	10	6	8		
CHFC1-CFCl ₂	70-74	6	8	7	Recov.	
CHClCCl ₂	84-88	30	26	30		
CFCl ₂ CFCl ₂	90-94	5	5	6	Possibly contam. with CF ₂ Cl-CCl ₃	
CHCl ₂ -CFCl ₂	112-116	6	9	6	Possibly contam. with CHFC1-CCl ₃	
Low polymers	128-208	9	8	11		
Residue	>208	7	10	5		
Total transitions		12	12	9		

¹ Weight percent of total crude product.

The vapor phase fluorination of trichloroethylene in which a molar reaction ratio of $\text{Fe}:\text{CHCl}=\text{CCl}_2:\text{N}_2$, (2:1:8) was used, yielded the results shown in Table 5.

Some of the products obtained in the fluorination of methane are listed in Table 6.

TABLE 6
Pure Compounds Obtained by Rectifying Fluorinated Methane (7)

Fract. of const. b. p. and mol. wt.	B. P. °C	Mol. Wt.	Compounds	B. P., °C		Mol. Wt.	
				Known	Found	Calcd.	Found
Mixture C	-89	94	→ CHF_3	-82	-82	70	72
			→ C_2F_6	-78	-79	138	137
Mixture D	-58	95	→ CH_2F_2	-52	-52	52	52
			→ C_3F_8	-38	-36	188	187
Mixture E	-89	85	→ CH_3F	-78	-78	34	35
			→ C_2F_6	-78	-79	138	138
Fluoroform ¹	..	..	CHF_3	-82	-82	70	71

¹ Small fraction, from an original distillation.

When benzene was fluorinated in vapor phase, the substances given in Table 7 were formed (8).

Higher yields of fluorinated compounds are obtained by first preparing partially fluorinated hydrocarbons, then chlorinating and treating them with hydrogen fluoride, and finally fluorinating by either of the last two methods just described. It is possible by this process to substantially convert paraffins to fluorocarbons. The paraffins are chlorinated photochemically in the liquid phase, then treated with hydrogen fluoride. This method makes possible high fluorine substitutions. These are then fluorinated with elemental fluorine.

The fluoroolefins are prepared by the method in which dichlorides or dibromides are formed, and then these compounds are converted to fluoroolefins with zinc. The fluoroolefins polymerize readily (9, 10).

TABLE 7
The Results Obtained by Fractionating Fluorinated Benzene (8)

Fraction	Observed B.P., °C	Mol. Wt.	Vol/100 hr Operation, cc.	Type	Product	Remarks
1	-128	88	10.0	Compound	CF ₄	
2	- 78	138	1.5	Compound	C ₂ F ₆	Quantity estimated
3	- 55	114	1.5	Azeotrope	..	Not as yet separated
4	- 36	188	3.0	Compound	C ₃ F ₈	
5	-5 to -3	236	1.0	Compound	C ₄ F ₁₀	Purified, b.p. -2, mol wt 238
6	22	246	4.0	Heterogeneous	..	B.p. -11 at 218 mm, carries C ₆ H ₆
7	48	246	13.0	Heterogeneous	..	B.p. 10-12 at 218 mm; carries C ₆ H ₆
8	61-63	220	6.0	Azeotrope	..	B.p. 15-17 at 170 mm; carries C ₆ H ₆
9	68	194	2.5	Azeotrope	..	B.p. 20° at 170 mm; carries C ₆ H ₆
10	74	...	3.0	Azeotrope	..	Carries much C ₆ H ₆
11	79	..	...	Heterogeneous	..	C ₆ H ₆ carries some product
12	80 up	...	...	Homogeneous	..	C ₆ H ₆ + residue. Almost dry at 85°

TABLE 8
The Physical Properties of the C_4F_8 Olefins and Their Dibromides

Compound	B.P., °C	n_D^{25}	d_4^{25}	Mol. Wt. Calcd. Found	Analysis			
					Carbon Calcd. Found	Fluorine Calcd. Found	Bromine Calcd. Found	
$CF_3CF_2CF_2CF_2$	+1		1.5443(0*)	200 198-202	24.0 24.3	76.0 75.5		
$CF_3CF_2CF_2CF_3$	0		1.5297(0*)	200 198-202	24.0 24.0	76.0 75.9		
$CF_3C(CF_3)CF_2$	+6.5		1.5922(0*)	200 198-202	24.0 24.1	76.0 76.1		
$C_2F_5CFBrCF_2Br$	95	1.3511	2.1279	360		42.2 41.5	44.4 44.5	
$CF_3CFBrCFBrCF_3$	96	1.3538	2.2673	360				
$(CF_3)_2CBrCF_2Br$	96			360 358		42.2 41.3	44.4 42.8	
$Br(CF_2)_4Br$	97	1.3495	2.0979	360		42.2 40.7	44.4 44.6	

TABLE 9
Heats of Combustion (12)

TETRAFLUOROETHYLENE

Run No.	1	2	4	5	6
Pressure, atm. abs.	3.63	3.63	3.63	3.63	3.63
Initial temp., °C	24.21	23.74	24.47	24.55	24.68
Temp. rise, °C	2.755	2.772	2.761	2.750	2.722
Energy equivalent, cal/°C	3404	3404	3404	3404	3404
Heat evolved, cal	9378	9435	9398	9361	9266
Heat from fuse, cal	28	28	28	28	28
Net heat, cal	9350	9407	9370	9333	9238
NaOH, moles a	0.2135	0.2135	0.2135	0.2135	0.2135
HCl, moles b	0.1248	0.1260	0.1248	0.1257	0.1252
HCl, moles c	0.0624	0.0618	0.0636	0.06200	0.0626
C ₂ F ₄ , moles					
to COF ₂ 1/4 (a-b-c)	0.0066	0.0064	0.0063	0.0065	0.0064
to CO ₂ +CF ₄ c-1/2 (a-b-c)	0.0492	0.0490	0.0510	0.0491	0.0498
Sum	0.0558	0.0554	0.0573	0.0556	0.0562
Corrected for residual gas	0.0580	0.0576	0.0596	0.0578	0.0584
Heat of combustion, cal/g C ₂ F ₄	1612	1633	1572	1615	1582
Fraction to COF ₂	0.188	0.131	0.110	0.116	0.114
Mean heat of combustion, cal/g		1603 ± 28.9			
Mean fraction to COF ₂		0.1178 ± 0.0089			

HEXAFLUOROPROPYLENE

Run No.	1	2	3	4
Pressure, atm. abs.	2.36	2.36	2.36	2.36
Initial temp., °C	24.28	24.64	24.66	24.16
Temp. rise, °C	2.261	2.255	2.250	2.272
Energy equivalent, cal/°C	3404	3404	3404	3404
Heat evolved, cal	7696	7676	7659	7734
Heat from fuse, cal	28	28	28	28
Net heat, cal	7668	7648	7631	7706
NaOH, moles a	0.1994	0.1994	0.1994	0.1994
HCl, moles b	0.1151	0.1154	0.1154	0.1137
HCl, moles c	0.0590	0.0595	0.0595	0.0606
C ₂ F ₄ , moles				
to COF ₂ 1/4 (a-b-c)	0.0063	0.0061	0.0061	0.0063
to CO ₂ +CF ₄ c-1/2 (a-b-c)	0.0463	0.0472	0.0472	0.0480
Sum	0.0526	0.0533	0.0533	0.0543
Corrected for residual gas	0.0540	0.0547	0.0547	0.0557
Heat of combustion, cal/g C ₂ F ₄	1420	1398	1395	1384
Fraction to COF ₂	0.120	0.115	0.115	0.115
Mean heat of combustion, cal/g		1399 ± 30.6		
Mean fraction to COF ₂		0.1163 ± 0.0035		

TABLE 9 (continued)
Heats of Combustion

PERFLUOROCYCLOBUTANE

Run No.	1	2	3	4	5
Pressure, atm. abs.	2.38	2.04	2.04	2.04	2.04
Initial temp., °C	23.87	24.21	24.76	23.79	24.39
Temp. rise, °C	3.144	2.644	2.633	2.617	2.622
Energy equivalent, cal/°C	3404	3404	3404	3404	3404
Heat evolved, cal	10702	9000	8963	8908	8925
Heat from fuse, cal	28	28	28	28	28
Net heat, cal	10674	8972	8935	8880	8897
NaOH, moles a	0.3202	0.2135	0.2135	0.2135	0.2135
HCl, moles b	0.1979	0.1165	0.1128	0.1130	0.1135
HCl, moles c	0.0867	0.0680	0.0711	0.0706	0.0707
C ₂ F ₄ , moles					
to COF ₂ 1/4 (a-b-c)	0.0089	0.0073	0.0074	0.0075	0.0073
to CO ₂ +CF ₄ c-1/2 (a-b-c)	0.0689	0.0535	0.0563	0.0556	0.0560
Sum	0.0778	0.0608	0.0637	0.0631	0.0633
Corrected for residual gas	0.0810	0.0632	0.0662	0.0656	0.0658
Heat of combustion, cal/g C ₂ F ₄	1318	1420	1350	1354	1352
Fraction to COF ₂	0.109	0.119	0.116	0.119	0.115
Mean heat of combustion, cal/g		1359 ± 38.8			
Mean fraction to COF ₂		0.1156 ± 0.0046			

Table 10 lists some of the properties of perfluoro ethers and amines (11).

TABLE 10
Properties of Fluorinated Liquids

Ethers	Formula	B. P., °C	F. P., °C	d ₂₅	n _D ²⁵
Perfluoromethyl	(CF ₃) ₂ O	-59		..	...
Perfluoroethyl	(C ₂ F ₅) ₂ O	1		..	...
Perfluorobutyl	(C ₄ F ₉) ₂ O	101		1.71	1.261
Perfluorohexyl	(C ₆ F ₁₃) ₂ O	172	-57 glass	1.81	1.278
Perfluoro C ₄ cyclic	c-C ₄ F ₈ O	1		..	...
Perfluoro C ₆ cyclic	c-C ₆ F ₁₂ O	55		1.68	1.263
Perfluoro C ₈ cyclic	c-C ₈ F ₁₆ O	103		1.77	1.277
Perfluoromethyl perfluorobutyl	CF ₃ OC ₄ F ₉	36	-140 glass	1.58	1.240
Perfluoromethyl perfluorocyclohexyl	CF ₃ OC ₆ F ₁₁	80	-104 glass	1.74	1.273

TABLE 10 (continued)
Properties of Fluorinated Liquids

Tertiary Amines	Formula	B. P., °C	M. P., °C	d ₂₅	n _D ²⁵
Triperfluoromethyl	(CF ₃) ₃ N	-11		..	...
Triperfluoroethyl	(C ₂ F ₅) ₃ N	69		1.75	1.262
Triperfluoropropyl	(C ₃ F ₇) ₃ N	129		1.83	1.278
Triperfluorobutyl	(C ₄ F ₉) ₃ N	177	-25	1.87	1.291
Triperfluorohexyl	(C ₆ F ₁₃) ₃ N	256	28	1.93	1.303
Diperfluoroethylperfluoropropyl	(C ₂ F ₅) ₂ N(C ₃ F ₇)	91	-100 glass	1.76	1.269
Diperfluoropropylperfluoroethyl	(C ₃ F ₇) ₂ N(C ₂ F ₅)	111		1.79	1.273
N, N-Diperfluoroethylperfluorocyclohexylmethyl	C ₆ F ₁₁ CF ₂ N(C ₂ F ₅) ₂	163		..	1.304

Fluoroaromatics have been prepared by the following method: Bromine trifluoride and hexachlorobenzene are reacted with pentachlorobenzotrifluoride (C₆Cl₅-CF₃). This produces a complex mixture of perhalogenated fluorochlorobromonaphthenes that are separated by precision fractionation. Dehalogenation is then carried out with zinc dust and alcohol. The products obtained are fluorobenzene (C₆F₆) and fluorotoluene (C₆F₅-CF₃).

Relatively unreactive fluorocarbon derivatives have been prepared such as fluorocarbon hydrides, chlorides, oxides, and nitrides, which have proved useful in providing an additional range of properties to the inert fluorocarbons. Fluorocarbon derivatives interesting for their functional groups are the fluoroxy fluorocarbons, the fluorocarbon bromides, iodides, and carboxylic acids. A fluorocarbon derivative is a compound in which one or more but not most of the fluorine atoms have been replaced by other atoms or groups of atoms. An example is fluorocarbon carboxylic acid (C₃F₇CO₂H).

Faurote et al. (13) have partially fluorinated a number of esters and ethers and have tabulated a number of their physical properties. From these studies, they postulate the following generalizations regarding their oxidation stabilities.

"Esters of dibasic acids and fluoroalcohols have better oxidation stabilities than do analogous esters of dibasic acids and alkanols, because of the resistance of the fluorinated carbon chain to oxidative attack.

"Shortening the hydrocarbon chain of the dibasic acid component of the diester leads to additional gains in stability as the probability of oxidative attack is reduced.

"Lengthening the fluorocarbon chain of the alcohol component of the diester results in compounds of increased stability because of the shielding action by these groups. Such shielding would be expected to diminish with increased thermal agitation.

"Increasing the number of fluorocarbon chains provides more effective shielding for the labile methylene groups.

"Alkyl dibasic acid esters of fluoroalcohols are more oxidation-stable than the analogous diethers because of the greater strength of the ester linkages and the shielding action of the carbonyl oxygens.

"Diesters of fluoroalcohols with dibasic acids having conjugated ring structures are more stable than aliphatic straight chain dibasic acid esters.

"No discernible differences could be detected in the oxidation stabilities of esters derived from fluoroalcohols with either $-\text{CF}_3$ or $-\text{CF}_2\text{H}$ terminal groups."

The vigorous development of fluorine compounds during World War II revealed their prospects for peacetime use in many industrial fields, such as heat transfer and dielectric media, fire extinguishers, turbine impellents, high temperature lubricants, thermal and chemical resistant plastics, dyes, insecticides, fungicides, germicides, fireproofing compounds, etc. The exceptional solvent characteristics of the fluorine compounds opened further possibilities in the field of solvent extractions. The future of fluorine compounds is viewed with rare optimism and it is anticipated that processes will be developed to produce them more cheaply and that special equipment will also be made to accommodate the special properties of these compounds.

The first large-scale use of fluorocarbon propellants and solvents took place with the Allied Armed Forces in the Pacific Theater of Operations during World War II. These compounds prevented our forces

from being attacked and out-flanked by still another and more deadly enemy, the myriads of disease-bearing insects. The effectiveness demonstrated by these compounds in destroying insects soon resulted in the appearance of similar products for home consumption. Since these products were compressed in containers and the contents easily released in the form of a spray, they were called aerosols from a composite word meaning "air" and "dissolve." It was not long before the aerosols were familiar throughout the world.

At present, the "Freons" and "Genetrons" are the most widely used of the fluorocarbons. Other fluorochemicals are still in the class of chemical specialties. Some of the high molecular weight compounds commercially available which make ideal transfer liquids are perfluoromethylhexane, perfluorodimethylhexane, monochloropentadecafluorodimethylcyclohexane, and the compounds classed as kerosenes and oils with the approximate compositions of $C_{12}F_{26}$, $C_{14}F_{30}$, $C_{20}F_{42}$, $C_{21}F_{44}$.

As lubricants, they are of particular value where highly corrosive conditions exist, exhibiting such properties as low adhesion and cohesion, strong resistance to high temperatures and chemical reaction. They do not form unsaturated compounds that polymerize to form gums, a major disadvantage of the hydrocarbon lubricants. They have high temperature coefficients of viscosity and high freezing points that seriously limit their usefulness. But research is being carried on to overcome these difficulties. These compounds are insoluble in most of the ordinary solvents but most of them are soluble in trifluorochloroethylene (C_2F_3Cl). They are used as plasticizers for the perfluoroethylene polymer. With the polymerization of perfluoro or fluorochlorocarbons, such valuable products as high viscosity oils, greases, waxes, and high-resistant plastics are made. The perfluorocarbons which are completely fluorinated hydrocarbons are not in direct competition with oils, greases, and solvents in common use, since their cost is still

very high. In 1950 this ranged from \$3.50 to \$4.50 per pound for hexane derivative and from \$16 to \$18 per pound for fluorinated petroleum derivatives. At present, interest is limited to applications where their extreme properties of inertness are required to resist the attack of strong oxidizing acids or high temperatures. The severe operational requirements of modern military and industrial equipment are making continued use of these lubricants and hydraulic fluids.

The "Freons," a trade name for the chloro-fluorocarbons (E. I. duPont de Nemours), are the most important group of organic fluorine compounds and are widely used commercially as refrigerants. They are also used as propellants in aerosol bombs, as solvents, inert dispersing agents, fire extinguishers, high-voltage insulation, and x-ray equipment. The "Freons" are produced with a wide volatility range by fluorine substitution of the hydro and hydrochloro compounds, which influences the boiling point of the parent substance. Their important properties are: low toxicity, nonflammability, non-combustibility, freedom from odor, chemical stability, and they do not affect foodstuffs. The production of "Freons" is so extensive that their present price is about 25 cents a pound. The "Freons" are soluble in, and solvents for a wide variety of organic compounds. They are miscible in all proportions with most of the common organic solvents in the liquid phase over a wide range of temperatures. There are instances where two liquid layers may be formed at low temperatures. Their solubility is usually high for similar types of compounds and low for compounds with very different chemical structures. They tend to be better solvents for hydrocarbons and halogenated compounds and have very low solubility for highly polar solvents such as glycols. Fluorinated compounds containing other halogens are usually better solvents than the completely fluorinated compounds. Generally, compounds with low molecular weights are more soluble in the "Freons" than those with high molecular weights. The "Freons" vary in their sol-

vent power depending on their chemical structure, and have been observed to decrease in solvent power in the following order:

"Freon-21">"Freon-11">"Freon-113">"Freon-22">"Freon-12">"Freon-114".

The "Freons" are produced by a modified Swarts reaction in which carbon tetrachloride is fluorinated with hydrogen fluoride in the presence of antimony pentachloride. Of these compounds, "Freon 12," dichlorodifluoromethane (CCl_2F_2), is the most important refrigerant. "Freon 11," trichloromonofluoromethane, is produced in smaller quantities because of more limited usefulness. It is used as a diluent in certain propellant compositions.

Other well-known refrigerant and propellant compounds are the "Genetrons" (General Chemical Division, Allied Chemical and Dye Corporation) such as "Genetron 100," 1, 1-difluoroethane, and "Genetron 101," 1-chloro-1, 1-difluoroethane, and the Isotrons. Other commercial refrigerants are "Carrene 7" which is a blend of "Genetron 100" and "Freon 12," and "Kulene 131," bromotrifluoromethane, a low temperature refrigerant which recently appeared on the market. Some of the "Genetrons" are similar in chemical structure to the "Freons." Their chemical composition determines their physical and chemical properties as well as their applications.

The tendency of fluorine compounds to polymerize has given rise to a number of perfluoro and perfluorochloropolymers remarkable for the new and promising possibilities which they opened to the plastic industry. Of major importance are the two plastics known commercially as "Teflon," polytetrafluoroethylene, and "Kel-F," polychlorotrifluoroethylene, in which compounds all the hydrogen atoms are replaced by halogen atoms. Some of the unusual properties of these plastics are their wide range of temperature resistance ("Kel-F" withstands temperatures from -100 to over 350°F and "Teflon" up to 500°F), resistance to fuming nitric acid, aqua regia,

TABLE 11
Liquid and Saturated Vapor Enthalpies

Temp., ° C.	Heat of Vaporization, Cal./Gram-Mole	Enthalpy, Cal./Gram-Mole		
		Liquid	Satd. vapor	Ideal gas
CH ₃ CHF ₂				
-40.0	5230	0	5230	5250
-20.0	5060	428	5510	5570
0.0	4870	860	5730	5840
20.0	4620	1340	5960	6160
40.0	4250	1900	6140	6490
60.0	3760	2510	6270	6840
80.0	3090	3220	6300	7200
100.0	2050	4050	6100	7580
113.5	0	5500	5500	7840
CH ₂ CF ₂ Cl				
-40.0	5740	0	5740	5760
-20.0	5500	590	6090	6130
0.0	5230	1200	6430	6510
20.0	4940	1810	6750	6900
40.0	4590	2440	7030	7300
60.0	4180	3100	7280	7720
80.0	3690	3760	7450	8150
100.0	3110	4400	7510	8610
120.0	2330	5230	7460	9080
CH ₃ CF ₃				
-40.0	4510	0	4510	4570
-20.0	4230	540	4770	4890
0.0	3920	1080	5000	5230
20.0	3540	1680	5220	5610
30.0	3300	2000	5300	5800
45.0	2870	2530	5400	6100
60.0	2070	3230	5300	6390
CF ₃ CFCl ₂				
-40	5550	0	5550	5560
-20	5490	590	6080	6090
0	5380	1200	6580	6630
20	5220	1940	7060	7170
40	4980	2560	7540	7740
60	4640	3350	7990	8320
80	4230	4160	8390	8900
100	3670	5060	8730	9490
120	2930	6010	8940	10260
145.5 (T critical)	0	8060	8060	10910
CH ₂ =CF ₂				
-40	3150	0	3150	3320
-20	2780	390	3170	3580
-10	2550	570	3120	3710
0	2280	720	3000	3840
+10	1930	850	2780	3975
+20	1430	970	2320	4120
+25	980	1030	2010	4195
CHCl=CF ₂				
-40.0	5620	0	5620	5620
-20.0	5400	530	5930	5930
0.0	5130	1060	6190	6260
20.0	4810	1650	6460	6590
40.0	4420	2290	6710	6940
60.0	3980	2950	6930	7290
80.0	3380	3710	7090	7870
100.0	2420	4700	7120	8050
120.0	800	6090	7030	8590

resistance to exposure to air at 200°C, zero water absorption, insolubility in solvents, low wettability of surface, extremely low brittle points, high softening points, high electrical resistance, and low dielectric loss factor. They find extensive use in the electrical industry as coatings for magnet wire, insulation for coaxial cable, and supports for radar and FM antennas. The low adhesion of "Teflon" and "Kel-F" makes them particularly valuable in conveyor belts where sticky materials are carried, on breadmaking machinery, and on machinery for heat-sealing plastic films.

Low molecular weight liquid products are made by polymerizing chlorotrifluoroethylene and then fluorinating the chainends to make them more stable. These lubrication oils are known commercially as liquid "Kel-F," fluoroethenes, "Fluorolubes," and halocarbon products. Completely fluorinated ethers and tertiary amines are of interest as coolants in coaxial cables for the transmission of high-frequency and microwave energy in aircraft. These compounds are found to be stable at temperatures of 400°C and above, their breakdown voltages are 50 to 100 per cent higher than hydrocarbon or Askarel-type insulating liquids, and they do not break down even on repeated arcing. They have low dielectric constants, low dissipation factor, are nonflammable and noncorrosive, and do not carbonize.

Fluorinated higher olefins have recently been prepared by the pyrolysis of sodium salts of perfluoro acids. These compounds and their polymers have been used to develop a variety of products of merit. Perfluoro olefins have been reacted with alcohols to obtain ethers of exceptional solvent power, which are compatible with both hydrocarbons and highly fluorinated compounds.

Interest in perfluoro acids has been considerable because of rare properties that distinguish them. They are superior to any other known surface-active agent for lowering the surface tension of water. They are chemically stable, even in white fuming

nitric acid and in 90 per cent hydrogen peroxide, and their boiling points are about 50°C lower than the corresponding hydrocarbon acids. They have good solubility, their acidity equals the mineral acids, and they are nonoxidizable and nonoxidizing. Their properties indicate possible uses as foaming and dispersing agents.

Trifluoroacetic acid was of vast importance to the Atomic Energy Program during World War II. It was used in preparing thenoyl trifluoroacetone, a fluorine compound necessary for the purification of certain rare metals. The electrofluorination process is a simpler and more direct method of producing the higher perfluoro acids.

Fluorine-containing dyes are commanding serious commercial attention. They were used extensively in Germany before and during World War II. Over 100 tons of azo dyes such as Naphthol AS, containing the CF_3 group, were sold in that country during 1939. Fluorine-containing vat dyes were known prior to the war, the vat dye Indanthrene Blue CLB having been used in producing Flieger gray for the German Air Force. Eastone Red GLF, an important fluorine azo dye in the United States, used as a dischargeable red azo dye for cellulose ester fiber, is considered superior in light fastness to some of the other azo dyes.

The insecticide field has become familiar with such effective fluorine-containing compounds as sodium monofluoroacetate better known as rodenticide 1080, a powerful rat poison, the difluoro analog of DDT known as DFDT, difluorodiphenyltrichloroethane, and others. Compared with DDT, DFDT is found to be superior against flies, beetles, and bedbugs, but suffers by comparison in regard to its greater volatility.

The toxicity and physiological action of the fluorocarbons are not yet fully understood. They have shown an extreme range in toxicity from the least active organic compounds among the "Freons" to the highly poisonous monofluoroacetic acid used as a rat

poison, and monofluoroethanol, a fluoroalcohol. The alkyl fluorophosphonates are another highly toxic group of fluorine compounds which, when inhaled, cause respiratory failure due to their anticholinesterase activity.

Fluorine compounds are being investigated by many industries seeking to benefit from the unique characteristics that can be created by fluorination. As yet these compounds represent a small part of the chemical industry, but quantity production has reached considerable proportions. The acceleration of fluorine research first activated by the war has now tapered off. The vast reservoir of practical and obtainable products, as visioned by those familiar with the behavior of these compounds, however, continues to stimulate an interest in this phase of chemistry that will continue to match the promise they offer.

A recent announcement has been made of plans to construct a new plant which will increase the United States capacity for the production of fluorinated gases to 300 million pounds a year. Other fluorine-containing products will be explored by this plant with the prospect of including agricultural chemicals, surface-active agents, and lubricants.

In Tables 12 through 19 the properties of fluorocarbons have been compared with their corresponding hydrocarbons.

TABLE 12

Boiling Points (760 mm) of Fluorocarbon and Hydrocarbon n-Alkyl Halides¹ (14)

Halogen	CH ₃	CF ₃	C ₂ H ₅	C ₂ F ₅	C ₃ H ₇	C ₃ F ₇	C ₅ H ₁₁	C ₅ F ₁₁
Cl	-23.73	-82 ²	13.1	-38	46.60	-2	108.4	59.5
Br	4.5	-59	38.40	-21	71.00	12	127.9	73.9
I	42.50	-22.5 ³	72.30	12.5	102.45	41.2	154.2	94.4

¹ The values for the hydrocarbon derivatives in this table and those following were taken from Beilstein's "Handbuch der organischen Chemie," the "International Critical Tables," the Landolt-Boernstein "Physikalisch-chemische Tabellen," and J. Timmerman's book "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., 1950.

² Ruff and Keim, Z. anorg. u. allgem. Chem., 201, 255 (1931).

³ Banks, Emeleus, Haszeldine, and Kerrigan, J. Chem. Soc., 2188 (1948).

TABLE 13
Densities of Fluorocarbon n-Alkyl Halides (14)

Halogen	CF ₃ X		C ₂ F ₅ X		C ₃ F ₇ X		C ₅ F ₁₁ X	
	d ₄ ^t	t, °C	d ₄ ^t	t, °C	d ₄ ^t	t, °C	d ₄ ^t	t, °C
Cl	1.726 ¹	-130	1.6914	-78.5	1.6605	-33.5	1.7150	0.0
	1.296 ²	-30	1.5678	-42.2	1.5572	0.0	1.6450	25.8
Br	1.94 ³	-54	1.9492	-32.2	1.9845	-32.2	1.9324	0.0
	1.78 ³	-18	1.8098	0.0	1.8746	0.0	1.8522	28.4
I	2.5485 ⁴	-78.5	2.1605	0.0	2.1306	0.0	2.1141	0.0
	2.3608 ⁴	-32.5	2.0718	23.5	2.0337	28.5	2.0349	27.8

¹ Ruff, and Keim, Z. anorg. u. allgem. Chem., 201, 255 (1931).

² Kinetic Chemicals, Technical Bulletin Freon Compounds.

³ Minnesota Mining and Manufacturing Co., Technical Bulletin, Trifluorobromomethane.

⁴ Nodiff, Grosse, and Hauptschein, unpublished data.

TABLE 14
Normal Boiling Points of Fluorocarbon and Hydrocarbon
Polymethylene Dihalides (°C) (14)

Halogen	X(CF ₂) ₂ X	X(CH ₂) ₂ X	X(CF ₂) ₃ X	X(CH ₂) ₃ X	X(CF ₂) ₄ X	X(CH ₂) ₄ X
Cl	3.8 ¹	83.5	35.7	125		161-163
Br	46.4 ¹	131.65	74.2	167.3		197-198
I	113 ²		131	224	150	

¹ Locke, Brode, and Henne, J. Am. Chem. Soc., 56, 1726 (1934).

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

TABLE 15
Molar Refractions of Fluorocarbon and Hydrocarbon
Polymethylene Dihalides (14)

Halogen	X(CF ₂) ₂ X	X(CH ₂) ₂ X	X(CF ₂) ₃ X	X(CH ₂) ₃ X	X(CF ₂) ₄ X	X(CH ₂) ₄ X
Cl	21.34	20.98	26.52	25.11		30.16
Br		26.95	31.90	31.18		
I	38.88		42.19	41.83	46.98	46.43

TABLE 16

Densities and Molecular Volumes at the Normal Boiling Point of
Fluorocarbon and Hydrocarbon n-Alkyl Halides (14)

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

TABLE 17

Molar Volumes at 20°C of Fluorocarbon and Hydrocarbon
Polymethylene Dihalides (14)

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

TABLE 18
Indices of Refraction and Molar Refractions of Fluorocarbon and Hydrocarbon
n-Alkyl Halides (14)

Compound	H		F		H	F
	n_D^t	t	n_D^t	t	M. R.	$\frac{LL}{D}$
CX ₃ Cl	1.3712	-23.7			11.62	
CX ₃ Br	1.4269	4.5			14.64	
CX ₃ I	1.5311	20	1.3710	-29.8	19.27	18.90
			1.3790	-42.2		
C ₂ X ₅ Cl	1.3724	13.1	1.2678	-42.2	16.29	16.60
C ₂ X ₅ Br	1.4130	38.4	1.2966	-29.8	19.10	18.97
			1.3040	-42.2		
C ₂ X ₅ I	1.5137	20	1.3378	0.5	24.25	23.74
			1.3636	-42.2		
C ₃ X ₇ Cl	1.3886	20	1.2781	-29.8	20.80	21.60
			1.2837	-42.2		
C ₃ X ₇ Br	1.4349	20	1.3070	-29.8	23.75	24.05
			1.3131	-42.2		
C ₃ X ₇ I	1.5057	20	1.3391	0.5	28.87	29.07
			1.3624	-42.2		
C ₅ X ₁₁ Cl	1.4119	20	1.2736	25.4	28.84	31.77
			1.2845	0.0		
C ₅ X ₁₁ Br	1.4444	20	1.2920	27.8	32.98	34.19
			1.3042	0.0		
C ₅ X ₁₁ I	1.4955	20	1.3243	31.5	38.30	39.18
			1.3389	0.5		

TABLE 19
Calculated Properties of n-C₄F₉X and n-C₆F₁₃X (14)

	N. B. P., °C	Molar Volume at B.P.	Molar Refraction	d at ¹ N.B.P.	n_D^1 at N.B.P.
n-CF ₃ (CF ₂) ₃ Cl	29	164	26.62	1.55	1.258
n-CF ₃ (CF ₂) ₃ Br	43	169	29.2	1.77	1.275
n-CF ₃ (CF ₂) ₃ I	69	181	34.1	1.91	1.302
n-CF ₃ (CF ₂) ₅ Cl	87	227	36.7	1.56	1.256
n-CF ₃ (CF ₂) ₅ Br	101	232	39.2	1.72	1.269
n-CF ₃ (CF ₂) ₅ I	120	246	44.2	1.81	1.287

¹ Values calculated from molar volumes and molar refractions given in the above table.

So extensive is the use of elastomers, that particular importance is given to the data in Table 20 showing how they are affected by halohydrocarbons.

TABLE 20
Swelling of Elastomers in Halohydrocarbons (15)

Halohydrocarbon	Increase in length (maximum) (room temperature), %						
	Neoprene type GN	Buna N type	Rubber	GR-S	Polysulfide type	GR-I	Neoprene type RT
Carbon tetrachloride CCl ₄	36	11	44	31	14	50	41
Chloroform CHCl ₃	43	54	45	32	91	45	50
Methylene chloride CH ₂ Cl ₂	37	52	34	26	59	23	44
Methyl chloride CH ₃ Cl	22	35	26	20	11	16	...
Freon-21 CHCl ₂ F	28	48	34	49	28	24	29
Freon-22 CHClF ₂	2.4	26	6	4.4	3.5	1.2	-0.2
Freon-31 CH ₂ ClF	9	38	12	9.6	8.4	2.6	8
Freon-32 CH ₂ F ₂	0	2.7	0	0	0	0	0
Freon-11 CCl ₃ F	17	6	23	21	2.1	41	16
Freon-12 CCl ₂ F ₂	0	2	6	3	0.8	5.6	-1.7
Freon-13 CClF ₃	0	1.3	1	0.5	0	...	...
Freon-112 CCl ₂ FCCl ₂ F	19	6.6	32	23	1.5	43	...
Freon-114 CClF ₂ CClF ₂	0	0	2.2	1.5	0	2.2	...
Freon-115 CClF ₂ CF ₃	0	0	0	0	0.2	0	...
Freon-218 CF ₃ CF ₂ CF ₃	0	0	0	0	0	0	...
Freon-C316	0	0	1	0	0	1.5	...
CF ₂ CClFCClFCF ₂							...
Freon-C318	0	0	0	0	0	0	...
CF ₂ CF ₂ CF ₂ CF ₂							...
Brom-113 CBrClFCBrF ₂	28	17	36	25	6.7	43	...
Brom-114 CBrF ₂ CBBrF ₂	6.6	7.1	26	15	0.7	...	...
CB CH ₂ ClBr	39	53	34	25	99	14	48
n-Butane C ₄ H ₁₀	2.7	1.2	16	7.8	0	20	0.5
n-Pentane C ₅ H ₁₂	3.9	1.2	20	9.4	0	29	0.7

* Polyvinyl alcohol.

TABLE 21
Derivatives of Benzene and Toluene (16)

Formula	Boiling Point °C	Mm	Melting Point, °C	n _D ²⁰	d ₄ ²⁵	% Cl		% F		Mol. Wt.	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
Benzene											
C ₆ F ₆	56.0-57.0	743	+6	1.3149	1.601	0.0	0.0	67.8	67.9	224.0	223.0
C ₆ F ₆	81.0-82.0	743	-13 to -11	1.3760	1.612	0.0	1.1	61.4	60.7	186.0	189.0
C ₆ ClF ₇	88.0-89.0	740	-60 to -65	1.3560	1.633	14.8	13.8	55.3	56.6	240.5	241.0
C ₆ Cl ₂ F ₈	112.5-113.5	750	-70	1.3748	1.719	24.1	23.0	51.5	53.5	295.0	286.0
C ₆ Cl ₂ F ₆	119.0-120.0	750	-25 to -30	1.4030	1.656	27.6	25.2	44.4	45.8	257.0	250.0
C ₆ ClF ₅	122.0-123.0	750		1.4256	1.568	17.5	16.1	46.9	45.4	202.5	200.0
C ₆ Cl ₃ F ₇	145.5	750	<-76	1.4013	1.774	34.2	34.3	42.7	42.4	311.5	311.0
C ₆ Cl ₃ F ₅	156.0-157.0	750	0 to +5	1.4466	1.692	39.0	36.2	34.8	33.8	273.5	259.0
Toluene											
C ₆ F ₅ (CF ₃)	103.5	740	<-70	1.3664	1.660	0.0	0.6	64.5	64.7	236.0	239.0
C ₆ Cl ₂ F ₇ (CF ₃)	128.5-129.5	750	<-70	1.3681	1.759	20.6	20.1	55.1	56.6	345.0	329.5
C ₆ ClF ₄ (CF ₃)	135.8-136.0	740	<-70	1.4043	1.700	14.1	14.2	52.7	52.4	252.5	249.5
C ₆ Cl ₃ F ₆ (CF ₃)	158.0-160.0	745	<-70	1.3930	1.792	29.5	29.2	47.4	29.2	361.5	359.0
C ₆ Cl ₂ F ₅ (CF ₃)	170.5-170.7	742	-59 to -58	1.4445	1.715	26.4	25.5	42.4	42.6	269.0	270.0

TABLE 22
Compounds Derived from p-Ethyltoluene (17)

Compound	Boiling Point °C	Mm	M.P., °C	n_D^{20}	d_4^{26}	Mol. Wt. Theo- retical	% Cl Theo- retical	% F Theo- retical
4-CCl ₃ C ₆ H ₄ C ₂ Cl ₅		...	115.0			396	71.7	0.0
4-CF ₃ C ₆ H ₄ C ₂ F ₅	128.5-128.7	746	-8.3	1.3690	1.4572	264	0.0	57.6
4-CF ₃ C ₆ H ₄ C ₂ F ₄ Cl	159.0-159.2	746	-13.0	1.4005	1.5291	277	12.6	47.5
4-CF ₃ C ₆ H ₄ C ₂ F ₃ Cl ₂	187.9-188.1	751	-2.4	1.4313	1.5184	297	23.9	38.4
4-CF ₃ C ₆ H ₄ C ₂ F ₂ Cl ₃	217.0-217.2	751	27.5		1.5610	313.5	34.0	30.3
4-CF ₃ C ₆ H ₃ ClC ₂ F ₄ Cl	184.8-185.0	751	No crystals	1.4275	1.5631	315	22.5	42.2
4-CF ₃ C ₆ H ₂ Cl ₂ C ₂ F ₃ Cl	211.0-211.2	751	1.2	1.4539	1.6586	349.5	30.5	38.5
4-CF ₃ C ₆ HClCl ₃ C ₂ F ₄ Cl	229.9-230.1	751	1.0	1.4828	1.7420	384	37.0	34.6
4-CF ₃ C ₆ Cl ₄ C ₂ F ₄ Cl	263.0-263.2	751	56.0			418.5	42.4	31.8
4-CF ₃ C ₆ H ₃ ClC ₂ F ₅	154.0-154.2	748	1	1.3980	1.5436	298.5	11.9	50.9

1 Glass at -70°C.

TABLE 23
Physical Constants and Halogen Analyses of New Compounds Derived from p-Cymene and Cumene (18)

Compound	Boiling Point °C	M.P., °C	n_D^{20}	d_4^{25}	Mol. Wt. Theo- retical	% Cl Theo- retical	% F Theo- retical
4-CF ₃ C ₆ H ₄ -iso-C ₃ F ₇	130.0-130.3	-2.1	1.3861	1.4127	314	0.0	60.5
4-CF ₃ C ₆ H ₄ -iso-C ₃ F ₆ Cl	161.3-161.6	-61.0	1.4095	1.4346	330.5	10.7	51.9
4-CF ₃ C ₆ H ₄ -iso-C ₃ H ₅ Cl ₂	190.0-190.3	-60 ¹	1.4292	1.5243	347	20.5	43.8
4-CF ₃ C ₆ H ₄ -iso-C ₃ F ₄ Cl ₃	219.0-219.3	-40 ¹	1.4609	1.5617	363.5	29.3	36.6
4-CF ₃ C ₆ H ₄ -iso-C ₃ F ₃ Cl ₄	240.0-240.3	-30 ¹	1.4928	1.6163	380	37.4	30.1
4-CF ₃ C ₆ H ₃ Cl-iso-C ₃ F ₄ Cl ₃	236.1-236.4	-20 ¹	1.4780	1.5996	398	35.7	33.4
4-CF ₃ C ₆ H ₂ Cl ₂ -iso-C ₃ F ₄ Cl ₃	258.9-259.2	-10 ¹	1.4972	1.6180	432.5	41.0	30.8
4-CCl ₃ C ₆ H ₄ -iso-C ₃ Cl ₇		128.0			479	74.05	0.0
C ₆ H ₅ -iso-C ₃ F ₇	127.3-127.6	-10.3	1.4112	1.4875	246	0.0	54.1
C ₆ H ₅ -iso-C ₃ F ₆ Cl	157.1-157.4	-38.0 to 38.2	1.4495	1.5477	262.5	13.6	43.4
C ₆ H ₅ -iso-C ₃ F ₅ Cl ₂	186.0-186.3	-70 ¹	1.4730	1.6264	279	25.5	34.1
C ₆ H ₅ -iso-C ₃ F ₄ Cl ₃	215.0-215.3	-65 ¹	1.4884	1.5427	295.5	36.1	25.7
C ₆ H ₅ -iso-C ₃ F ₃ Cl ₄	238.2-238.5	-40 ¹	1.5140	1.5950	312	45.5	18.3
C ₆ H ₄ Cl-iso-C ₃ F ₃ Cl ₄	260.3-260.6	-25 ¹	1.5340	1.6592	346.5	51.2	16.4
C ₆ H ₃ Cl ₂ -iso-C ₃ F ₃ Cl ₄	282.5-282.8	-11 ¹	1.5625	1.6993	381	56.0	14.9

¹ Glass at indicated temperature.

TABLE 24
Physical Properties of Fluorinated Derivatives of Mesitylene (19)

Compound	B. P. °C	Mm.	M. P., °C	d_4^{25}	n_D^{25}	M. R. ¹ _D	A. R. ² _F	% Cl Calcd. Found	% F Calcd. Found
$C_6H_2F(CH_3)_3$	166.6	744	-36.7	0.9745	1.4809	40.343	1.157	0.0 0.0	
$C_6H_3(CF_3)_3$	119.6	750	9.0	1.5139	1.3558	40.695	1.101	0.0 0.0	60.7 60.6
$C_6H_2F(CF_3)_3$	126.4	753	-10.2	1.5933	1.3555	41.103	1.137	0.0 0.0	63.4 63.3
$C_6H_2Cl(CF_3)_3$	152.4	750	-3.0	1.6316	1.3903	46.027	1.144	11.2 11.2	54.0 53.9
$C_6HCl_2(CF_3)_3$	71.1	5	61.0				...	20.2 20.5	48.7 48.1
$C_6Cl_3(CF_3)_3$	130-131	4	93-94				...	27.8 28.2	44.5 44.7
$C_6H_3(CCl_3)_3$	149-150	1	88.0-88.5				...	74.2 74.1	
$C_6H_2Cl(CCl_3)_3$		..	170-171				...	76.3 76.0	
$C_6HCl_2(CCl_3)_3$		..	142-144				...	78.2 78.0	
$C_6Cl_3(CCl_3)_3$		..	178-179				...	79.8 79.7	

¹ Molar refractivity at 25°C.

² Atomic refractivity at 25°C.

TABLE 25
Fluorinated Derivatives of Diethylbenzene (20)

Compound	B. P. at 750 Mm., °C	M. P., °C	d ₄ ²⁵	n _D ²⁵	% F		% Cl	
					Calcd.	Found	Calcd.	Found
1, 4-C ₆ H ₄ (C ₂ F ₅) ₂	138.5-139.0	17.1	1.5056	1.3590	60.5	60.3	0.0	0.0
1, 3-C ₆ H ₄ (C ₂ F ₅) ₂	134.5-135.0	-28.5	1.4938	1.3565	60.5	60.1	0.0	0.0
1, 4-C ₆ H ₄ (C ₂ F ₅)(C ₂ ClF ₄)	164.8-165.2	-7.5	1.5291	1.3878	51.8	52.4	10.8	10.9
1, 3-C ₆ H ₄ (C ₂ F ₅)(C ₂ ClF ₄)	160.5-161.0	-45.5	1.5219	1.3838	51.5	52.0	10.8	10.8
1, 4-C ₆ H ₄ (C ₂ ClF ₄) ₂	193.0-194.0	-13.5	1.5586	1.4140	43.8	44.0	20.5	20.6
1, 3-C ₆ H ₄ (C ₂ ClF ₄) ₂	190.0-190.5	No crystals	1.5517	1.4093	43.8	44.1	20.5	20.5

TABLE 26
Properties of Perfluoro Fused-Ring Compounds (21)

Name	Formula	B. P., °C	F. P., °C	d ₄ ²⁰	n _D ²⁰	% F		Mol. Wt. ¹	
						Calcd.	Obsvd.	Calcd.	Obsvd.
Perfluoronaphthalene	C ₁₀ F ₁₈	140	-7 to -10	1.9456	1.3118	74.0	73.4	462	464
Perfluoro-1-methylnaphthalene	C ₁₁ F ₂₀	161	Below -75	1.9606	1.3168	74.2	74.4	512	521
Perfluoro-2-methylnaphthalene	C ₁₁ F ₂₀	160-161	Below -60	1.9632	1.3164	74.2	74.7	512	517
Perfluoroacenaphthene	C ₁₂ F ₂₀	173	2 to 0	1.9883	1.3292	72.6	72.9	524	528
Perfluoroindane	C ₉ F ₁₆	116-117	-8 to -15	1.8838	1.3033	73.8	73.9	412	421
Perfluorofluorane	C ₁₃ F ₂₂	190	Below -40	1.9819	1.3264	72.9	74.1	574	571
Perfluorodimethylnaphthalenes	C ₁₂ F ₂₂	177-179	-30 to -40	1.9759	1.3200	74.4	74.0	562	567
Perfluorophenanthrene	C ₁₄ F ₂₄	205-206	Below -40	2.0197	1.3315	73.1	72.4	624	627
Perfluoroanthracene	C ₁₄ F ₂₄	211-213	76 to 81			73.1	71.3	624	603
Perfluorofluoranthene	C ₁₅ F ₂₅	235-239	-30 to -36	2.0598	1.3460	72.0	72.4	686	682

¹ Obtained by the Victor-Meyer vapor density method.

TABLE 27
Physical Properties and Analyses of Halobutanes (22)

Compound	M.P., °C	B.P., °C (745 Mm)	t, °C	d ₄ ^t	n _D ^t	% F		% Cl		Molar Refractivity	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
CH ₃ CH ₂ CFCH ₂	..	23.5	0	0.824	1.3492 ¹	..	..	..	..	19.5	19.5
CH ₃ CFCHCH ₃	..	26	..	...		..	..	..	..	..	..
CH ₃ CF ₂ CH ₂ CHF ₂	..	56.5	..	...		..	..	..	..	..	..
CH ₃ CF ₂ CHCHCl	..	72	27	1.157	1.3720	29.5	29.3	28.0	27.6	24.9	24.5
CH ₃ CFClCHClCH ₃	..	108	26	1.198	1.4163	13.1	12.7	48.9	48.2	30.4	30.3
CH ₃ CFClCH ₂ CH ₂ Cl	..	123	26	1.227	1.4220	13.1	13.0	48.9	50.1	30.4	30.3
CH ₃ CF ₂ CFClCH ₃	-19	53	22	1.215	1.3358	38.9	38.4	24.2	25.1	25.5	25.2
CH ₃ CF ₂ CH ₂ CHFCI	..	79-81	..	...		..	..	..	..	..	..
CH ₃ CF ₂ CH ₂ CF ₂ Cl	..	69	26	...	1.3340	46.2	46.6	21.5	21.5	..	..
CH ₃ CF ₂ CH ₂ CFCl ₂	..	102	26	1.357	1.3758	31.5	31.3	39.2	39.2	30.5	30.6
CH ₃ CF ₂ CCl ₂ CH ₂ Cl	..	140-141	32	1.443	1.4238	19.3	19.2	53.9	53.8	35.4	34.8
CH ₃ CF ₂ CCl ₂ CHCl ₂	..	165-167	32	1.556	1.4500	16.4	16.4	60.4	60.7	40.4	40.1
C ₄ HClF ₆	..	34	20	1.497	1.28	57.4	58.0	17.9	17.6	..	..
CH ₃ CF ₂ CHBrCH ₂ Br	-12	155-157	27	1.933	1.4594	15.1	13.7	(63.5	64.2) ²	36.3	35.7
CH ₃ CCl ₂ CCl ₂ CH ₃	174 ³		..	...		..	..	72.5	72.4	..	..

¹ t = 15°C.

² Bromine.

³ Sealed tube.

TABLE 28
Physical Properties of Aryloxy (Polychlorofluoro) Alkanes and -Alkenes (23)

Formula	B. P., °C		M. P., °C	d ₄ ²⁵	n _D ²⁰	Calculated		Analyses	
	740 mm ¹	4 mm ²				% Cl	% F	Mol. Wt.	Observed % Cl % F Mol. Wt.
C ₆ H ₅ OCF ₂ CHCl ₂	216.0	67.9	-23.5 to -24.0	1.3706	1.4789	31.2	16.7	227	31.2 17.4 224
2-CH ₃ C ₆ H ₄ OCF ₂ CHCl ₂	230.0	77.5-78.0 ⁴	-18.0 to -20.0	1.334	1.485	29.5	15.8	241	29.3 15.0 240
3-CH ₃ C ₆ H ₄ OCF ₂ CHCl ₂	230.5	77.9-78.4 ⁴	Sets to a glass	1.322	1.482	29.5	15.8	241	29.4 14.2 247
4-CH ₃ C ₆ H ₄ OCF ₂ CHCl ₂	233.5	79.8-80.3 ⁴	-13.0 to -16.0	1.320	1.481	29.5	15.8	241	29.5 15.5 238
3-CF ₃ C ₆ H ₄ OCF ₂ CHCl ₂	211.0	64.2-64.7 ⁴	Sets to a glass	1.485	1.437	24.5	32.2	295	24.6 33.0 304
C ₆ H ₅ OCF ₂ CH ₂ Cl	196.0	55.8	-50.0 to -52.5	1.2704	1.4777	18.4	19.7	192.5	18.4 20.1 191
2-CH ₃ C ₆ H ₄ OCF ₂ CH ₂ Cl	213.5	66.0	-32.0 to -35.0	1.2388	1.4758	17.2	18.4	206.5	17.1 18.7 206
3-CH ₃ C ₆ H ₄ OCF ₂ CH ₂ Cl	217.0	69.8-70.0	Sets to a glass	1.2325	1.4731	17.2	18.4	206.5	17.2 19.0 204
4-CH ₃ C ₆ H ₄ OCF ₂ CH ₂ Cl	216.5	69.6-70.2	Sets to a glass	1.2222	1.4732	17.2	18.4	206.5	16.9 18.9 208
3-CF ₃ C ₆ H ₄ OCF ₂ CH ₂ Cl	197.0	56.6-56.9	-41.0 to -43.0	1.4177	1.4255	13.6	36.5	260.5	13.4 37.1 261
C ₆ H ₅ OCF ₂ CHClCF ₃	188.0	47.3	-32.0 to -35.0	1.4112	1.4215	13.6	36.5	260.5	13.2 36.6 257
1-Naphthyl-OCF ₂ CHClCF ₃	278.5	105.0-106.0	-10.0 to -12.0	1.4220	1.5071	11.4	30.6	310.5	11.6 30.9 310
C ₆ H ₅ OCFCCl ₂	210.0	63.0	-42.0 to -44.5	1.3364	1.5162	34.3	9.2	207	34.2 9.0 206
C ₆ H ₅ OCFCHCl	189.5	49.7-49.8	-50.0 to -51.0	1.2271	1.5049	20.5	11.0	172.5	20.3 11.7 172
2-CH ₃ C ₆ H ₄ OCFCHCl	204.5	59.3	-38.5 to -39.0	1.1903	1.5057	19.0	10.2	186.5	18.9 10.6 185
3-CH ₃ C ₆ H ₄ OCFCHCl	209.0	64.0-64.4	Sets to a glass	1.1880	1.5031	19.0	10.2	186.5	18.7 10.5 186
4-CH ₃ C ₆ H ₄ OCFCHCl	212.5	63.6-64.2	-40.0 to -41.5	1.1854	1.5032	19.0	10.2	186.5	18.8 10.7 185
3-CF ₃ C ₆ H ₄ OCFCHCl	189.5	50.0-52.0	-63.0 to -64.0	1.3909	1.4454	14.8	31.6	240.5	14.4 31.9 243
C ₆ H ₅ OCFCClCF ₃	184.5	43.2-44.1	-53.0 to -56.0	1.3673	1.4513	14.8	31.6	240.5	14.6 31.4 236
1-Naphthyl-OCFCClCF ₃	275.0	102.0-103.0	10.5 to 13.0	1.3859	1.5295	12.2	26.1	290.5	12.6 26.3 284

¹ Absolute values accurate to 0.2°C.

² Observed values subject to errors incurred in measuring pressure with Zimmerli manometer.

³ Absolute values accurate to 0.5°C.

⁴ Estimated from vapor-pressure slide rule [Miles, Ind. Eng. Chem., 35, 1052-61 (1943)] by use of reduced-pressure boiling point data for C₆H₅OCF₂CHCl₂.

FLUOROTRICHLOROMETHANE

"Freon-11"

"Genetron" 11

CCl_3F

"Freon" MF

Trichlorofluoromethane

Trichloromonofluoromethane is a colorless liquid used as a solvent and propellant in insecticidal and paint formulations. It is miscible with the aliphatic and aromatic hydrocarbons, alcohols, glycols, esters, ketones, and many other types of solvents. It is more powerful in solvent action than "Freon-12," and, like the latter, it will completely dissolve many of the halogenated derivatives. Substances containing one or more oxygen atoms are less readily dissolved. Water is very sparingly soluble in this solvent.

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	23.8°C (74.8°F)
Critical pressure	635.0 psia 43.2 atm.
Critical temperature	198.0°C (388.4°F)
Density @ 70°F (21.1°C),	
Liquid	12.39 lb/gal 92.71 lb/cu ft 1.485 g/cc
Vapor (sat'd)	0.3342 lb/cu ft 5.353 g/liter
Dielectric constant	
Liquid @ 86°F (30°C)	2.28
Vapor (0.5 atm.) @ 79°F	1.0019
Diffusivity in air @ 77°F, 1 atm.	0.080 sq cm/sec 0.307 sq ft/hr
Freezing point	-168°F (-111.0°C)
Heat capacity @ 70°F,	
Btu (lb) (°F) or cal/g/°C	
Liquid	0.205
Vapor (sat'd)	0.134

Latent heat of vaporization @ B. P.	78.31 Btu/lb 43.51 cal/g
Molecular weight	137.4
Refractive index of liquid @ 79.7°F (26.5°C)	1.384
Relative dielectric strength @ 73°F (23°C), 1 atm., (nitrogen = 1)	3.1
Solubility of water @ 70°F (21.1°C)	0.009% by wt
Solubility in water @ saturation pressure, 70°F (21.1°C)	0.14 % by wt
Surface tension @ 77°F (25°C)	19.0 dynes/cm
Thermal conductivity @ 70°F (21.1°C) Btu/hr/ sq ft/°F/ft	
Liquid	0.0629
Vapor	0.00473
Viscosity @ 70°F (21.1°C)	
Liquid	0.438 centipoises
Vapor	0.0108 centipoises

TABLE 29

Solubility of Some Organic Compounds in Fluorotrichloromethane (24)

Compound	Temperature °C °F		Solubility of Compound (% by Wt.)
Aristo wax	25	77	5.6
Di(p-chlorophenyl) tri- chloroethane (DDT)	20	68	7.5
Di(p-methoxyphenyl) tri- chloroethane (methoxychlor)	Room temperature		7.2
Ethylene oxide	25	77	Miscible
Paraffin (M. P. 52°C)	25	77	31
Propylene glycol (1, 2)	25	77	0.09
Triethylene glycol	25	77	0.45

DICHLORODIFLUOROMETHANE**"Freon-12"** **CCl_2F_2** **"Genetron" 12**

This water-insoluble compound is a colorless, nonflammable gas with a faint ethereal odor. It is miscible with many solvents and is used as a solvent and propellant in varnish and paint remover formulations, and as refrigerants. New advances have been made in the field of insecticidal sprays by utilizing low-boiling solvents as a means of dispersing insecticides. Some of the more promising solvents giving a fine dry spray, while at the same time, free from fire hazard and toxicity, are dichlorodifluoromethane, methyl chloride, and a mixture of propane and dichlorodifluoromethane.

Dichlorodifluoromethane is miscible with such hydrocarbon solvents as: benzene, p-cymene, decahydronaphthalene, diethylbenzene, dihydronaphthalene, diphenylmethane, heptane, ligroin, α -methyl naphthalene, mineral oil, tetrahydronaphthalene, toluene, and xylene; with such halides as: amyl chloride, bromobenzene, bromochloromethane, bromoform, carbon tetrachloride, chlorobenzene, chloroform, ethyl bromide, ethylene chloride, methyl chloride, and methylene chloride; with such esters as: amyl acetate, benzyl benzoate, n-butyl acetate, butyl butyrate, dibutyl oxalate, dibutyl phthalate, dibutyl tartrate, diethyl phthalate, dimethyl phthalate, ethyl acetate, ethyl benzoate, ethyl lactate, ethyl oxybutyrate, ethyl phenylacetate, isoamyl benzoate, methyl salicylate, and phenyl acetate; with such alcohols as: amyl alcohol, n-butyl alcohol, tert-butyl alcohol, diacetone alcohol, ethyl alcohol, n-hexyl alcohol, methyl alcohol, phenyl ethyl alcohol, and n-propyl alcohol; with such ethers as: butyl benzyl ether, butyl carbitol, butyl "Cellosolve," "Cellosolve," "Cellosolve" acetate, dibenzyl ether, dibutyl ether, diethyl ether, dimethyl ether, dioxane, diphenyl ether, α -methyl naphthyl ether, and phenetole; such ketones as: acetone, aceto-

phenone, cyclohexanone, hexylmethyl ketone, methyl-ethylketone, methylisobutylketone, and methylp-tolyl ketone; and with such miscellaneous substances as: acetic acid, acetonitrile, benzaldehyde, benzonitrile, carbon disulfide, cyclohexanol, dimethyl aniline, diphenyl isothiocyanate, ethylene oxide, methyl aniline, methyl cyclohexanol, nitrobenzene, phenyl isothiocyanate, pyridine, and sulfur dioxide.

PHYSICAL PROPERTIES

Boiling point	-29.8°C -21.6°F @ 1 atm. press.
Critical density	0.554
Critical pressure	43.2 atm. 582 psia
Critical temperature	198.0°C 232.7°F
Freezing point	-111°C -247.0°F @ 1 atm. press.
Molecular weight	120.6
Specific gravity @ -30°C	1.486
Vapor pressure @ 70°F	84.8 psia
Kauri-butanol number @ 77°F (25°C)	18.0
DDT, g/100 g "Freon"	0.8 (77°F)
Solubility in water (g "Freon"/liter H ₂ O)	
Atm. press. (14.7 psia)	{ 0.28 @ 77°F (25°C), 0.14 @ 122°F (50°C)
At the propellant vap. press.	{ 1.9 (94.4 psia) @ 77°F (25°C) 1.8 (176.2 psia) @ 122°F (50°C)
Solubility of water (g H ₂ O/100 g "Freon")	0.0076 @ 70°F (21°C)

TABLE 30
Paint Remover Formulation (25)

Constituent	Composition (Wt.%)
Crude Scale Wax	2.0
Ethyl Cellulose, T-100	2.0
Methylene Chloride	39.0
Methanol	9.1
Cellosolve Acetate	9.6
"Triclene" Trichloroethylene	13.3
"Freon-12" Dichlorodifluoromethane	25.0

TABLE 31
Compatibility of "Freon" Propellants with Resin Solutions (25)

Composition of Resin Solution	Compatibility in grams of "Freon" Propellant/gram of Resin Solution	
	"Freon-11"	"Freon-12"
Alkyd		
"Aroplaz" 1365X 40%, Xylene 60%	5	1.8
"Aroplaz" 1365X 30%, Xylene 70%	..	1.8
"Aroplaz" 1365X 30%, Xylene 20%, mineral spirits 50%	..	1.3
"Glyptal" 2462 40%, Xylene 60%	5	1.6
"Glyptal" 2532 40%, mineral spirits 60%	4	1.5
"Glyptal" 2504 40%, mineral spirits 60%	..	4
"Beckosol" No. 23 20%, isopropyl alcohol 20%, methylisobutyl ketone 60%	2.3	0.8
Nitrocellulose		
RS- $\frac{1}{4}$ sec. 20%, isopropyl alcohol 20%, methylisobutyl ketone 60%	3.6	1.8
RS- $\frac{1}{2}$ sec. 20%, isopropyl alcohol 20%, methylisobutyl ketone 60%	3.6	2.2

TABLE 32

"Freon-12" Solubility Data at 32.0°C (89.6°F) and a Pressure of 52.1 psia

Compound	Grams of "Freon-12" per 100 cc of Compound
3,3'-Dichloro-n-propyl ether	22.0
Dichloro-isopropyl ether	25.8
2,3-Di- β' -ethoxy- β -ethoxy dioxane	19.6
Diethyl ether of tetraethylene glycol	25.8
Dimethyl ether of tetraethylene glycol	21.5*
Ethyl ether of diethylene glycol methoxy acetate	16.2
α -Fluoronaphthalene	23.6
4-Methyl-2-pentanol acetate	52.0
Trichlorobenzene	20.4

* Grams of "Freon-12" per 100 grams of Compound at 32.2°C (90°F).

TABLE 33

Solubility of "Freon-12" at 21.1°C (70.0°F) and One Atmosphere Pressure

Solvent	Wt. % "Freon-12"	Mol. Fraction "Freon-12"
Amyl chloride	13.1	0.12
Benzene	9.0	0.060
Bromobenzene	5.0	0.063
Bromoform	1.2	0.025
n-Butyl alcohol	8.5	0.054
Butyl butyrate	13.2	0.14
Carbon tetrachloride	5.2	0.063
Chloroform	5.5	0.052
α -Chloronaphthalene	3.9	0.052
Cyclohexanone	8.5	0.069
Diacetone alcohol	6.1	0.060
Dibutyl ether	14.1	0.15
Dibutyl oxalate	8.9	0.13
Dibutyl tartrate	6.3	0.12
Dichloroethyl ether	3.9	0.046
Diethyl aniline	7.2	0.093
Diethyl phthalate	4.7	0.082
Dioxane	6.9	0.054
Ethylene dichloride	4.7	0.039
Ethylene glycol butyl ether	7.2	0.070
Ethylene glycol ethyl ether	7.4	0.055

Table 33 (continued)

Solubility of "Freon-12" at 21.1°C (70.0°F) and One Atmosphere Pressure

Isoamyl benzoate	8.6	0.13
Methyl alcohol	5.7	0.015
Methyl salicylate	3.0	0.040
Nitrobenzene	4.1	0.039
Phenetole	7.4	0.070
Toluene	11.6	0.091
Xylene	11.3	0.095

FLUORODICHLOROMETHANE

"Freon-21"

CHCl₂F

Fluorodichloromethane is a gas at ordinary temperatures, insoluble in water but soluble in alcohol and ether. It is considered to be the best solvent in the "Freon" family because of the arrangement of its molecule in which there are one hydrogen and two chlorine atoms. This compound is found to be miscible with all of those compounds with which "Freon-12" is miscible, and it is a better solvent than the latter where limited solubility exists.

PHYSICAL PROPERTIES

Boiling point @ 760 mm -1 atm.	48.0°F (8.9°C)
Chlorides	None
Color	Clear and water-white
Critical pressure	750 lb/in. ² abs.
Critical temperature	353.3°F (178.5°C)
High-boiling impurities	Not more than 0.05% by vol.
Melting point	-211°F (-135°C)
Moisture	Not more than 0.005% by wt
Molecular weight	102.93
Odor	Ethereal and similar to carbon tetrachloride Odorless when mixed with air

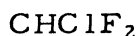
TABLE 34

"Freon-21" Solubility Data at 32.2°C (90.0°F) and a Pressure of 12.34 psia

Compound	Grams of "Freon-21" per 100 grams of Compound
Acetic acid	68.8
Acetyl acetone	102.3
Aniline	38.5
Anisole	67.3
Benzaldehyde	75
Cellosolve acetate	104
Cyclohexylamine	107
Decalin	27.2
3-3'-Dichloro-n-propyl ether	43.8
Diethyl ether of diethylene glycol	113
Diethyl phthalate	56.1
Diethylene glycol	28.5
Dimethyl aniline	69.5
Dimethyl ether of diethylene glycol	120
Dimethyl ether of tetraethylene glycol	111
Dioxane	107.7
Ethyl ether of diethylene glycol acetate	102
Ethylene glycol	10
Formamide	7.5
Heptaldehyde	97.9
Nitrobenzene	47.1
Phenol	26.9
Tetralin	47.5
Triethyl phosphate	113.2
Triethylene glycol	35.8
Trimethylene glycol	10.6

DIFLUOROCHLOROMETHANE

"Freon-22"



"Genetron" 141

Difluorochloromethane is a colorless, nonflammable gas with a faint ethereal odor. Its effectiveness as a solvent is due to the presence of both hydrogen and chlorine in the molecule. It is generally found to be a better solvent than "Freon-11," "Freon-12," or

"Freon-114" but is less powerful as a solvent than "Freon-21." The relative solvent power is dependent to a considerable extent upon the solute since in some tests "Freon-22" appears to be a poorer solvent than "Freon-11." The uses of this compound are as a solvent, propellant in aerosol formulations, as a low temperature vehicle for clay slurries, and for charging thermometers.

PHYSICAL PROPERTIES

Boiling point @760 mm	-40.8°C -41.44°F @ 1 atm. press.
Critical density	0.523 g/cc
Critical pressure	48.7 atm. 716 psia
Critical temperature	96.0°C 204.8°F
Chlorides	None
Freezing point	-160°C -256.0°F @ 1 atm. press.
DDT, g/100 g "Freon"	1.3 (70°F)
Heat content of the liquid @ 70°F (21°C)	30.99 Btu/lb
Kauri-butanol number @ 77°F (25°C)	24.5
Latent heat of vaporization @ 70°F (21°C)	80.50 Btu/lb
Liquid density @ 70°F (21°C)	1.209 g/cc
Moisture	0.005% by wt, max.
High-boiling impurities	0.05% by vol., max.
Molecular weight	86.5
Noncondensable gases	5.0% by vol., max., in vapor phase
Solubility in water (g "Freon"/liter H ₂ O)	
Atm. press. (14.7 psia)	{ 3.0 @ 77°F (25°C) 1.3 @ 122°F (50°C)
At the propellant vap. press.	{ 28 (152.7 psia) @ 77°F (25°C) 24 (284 psia) @ 122°F (25°C)

Solubility of water (g H ₂ O/100 g "Freon")	0.114 @ 70°F (21°C)
Vapor pressure @ 70°F (21°C)	137.2 psi, abs.
Odor	Ethereal and similar to carbon tetrachloride
Flammability	Practically nonflammable and nonexplosive
Toxicity	Group 5-A Classification of Underwriters' Laboratories Report, MH-3134-page 13
Melting point	-256°F -160°C

DIFLUOROCHLOROETHANE

"Genetron"-101



Difluorochloroethane is used as a solvent and as a propellant in aerosol formulations of cosmetics.

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	-9.2°C (15.4°F)
Flammable limits	9.0-14.8 vol. % in air
Freezing point	-131°C (-203°F)
Heat of vaporization @ B. P.	96.04 Btu/lb 5362 g cal/g mole
Liquid density @ 70°F	69.8 lb/cu ft
@ 130°F	64.1 lb/cu ft
@ 70°F	1.118 g/cu cm
@ 130°F	1.027 g/cu cm
Molecular weight	100.50
Saturated liquid viscosity @ -40°F	0.560 centipoise
@ 70°F	0.330 centipoise
@ 130°F	0.250 centipoise
Solubility of "Genetron" in water @ 70°F	0.19% by wt
Solubility of water in "Genetron" @ 70°F	0.048% by wt

Toxicity

Estimated grouping via rating
system of Underwriters' Labs.

Group 5-A (probably)

Vapor pressure @ 70°F
 @ 130°F

43.53 psia
111.8 psia

TABLE 35

Solubilities of Perfume Compounds in Propellants
At Room Temperature* (43)

	"Genetron" 101	"Genetron" 320	"Freon- 114"
Essential Oils (0.5% by wt.)			
Absolute Rose	I	I	I
Absolute Jasmin	I	I	I
Bergamot Italian	I	I	I
Geranium Reunion	S	S	S
Lavender, 40-42%	I	I	I
Lemon Italian	I	I	I
Orris Concrete Florentine	I	I	I
Patchouly Penang	I	I	I
Sandalwood East Indies	S	S	S
Sweet Basil	I	S	S
Ylang Bourbon	I	I	I
Aromatics (0.5% by wt.)			
Aldehyde C-11 (Undecylic)	S	S	I
Amyl Cinnamic Aldehyde	S	S	S
Benzyl Acetate	S	S	S
Cinnamic Alcohol Synthetic	S	I	I
Citronellyl Acetate	S	S	S
Hydroxy Citronellal	S	I	I
Ionone Alpha-White	S	S	S
Ionone Methyl-Extra	S	I	I
Linalool	S	S	S
Linalyl Acetate 90/92%	S	S	S
Ex Boise de Rose			
Methyl Hexyl Ketone	S	S	I
Phenyl Ethyl Alcohol	S	S	S
Tinctures: 4 oz./gal (25% by wt.)			
Ambergris Gray	I	I	I
Musk Tonquin Grain	I	I	I
Civet Abyssinian	I	I	I

S = Soluble

I = Insoluble

All essential oils and aromatics soluble in alcoholic solutions comprising
1 part oil, 24 parts SD Alcohol 39C and 75 parts propellant by weight.

*Data supplied by Dodge and Olcott, Inc.

TABLE 36
Solubilities of Essential Oils and Aromatic Chemicals
in Propellants at Room Temperature* (43)

Compound (1.0% by Wt.)	"Genetron" 101	"Freon-114"
Anise Star USP	S	C
Anisic Alcohol	I	I
Alpha Ionone	S	S
Bay Leaves	S	C
Benzyl Acetate	S	S
Cananga Native	S	C
Clove Buds USP	S	C
Eugenol	S	I
Jasmin Absolute	S	I
Lavender, 38-42%	S	I
Linalool	S	C
Methyl Ionone	S	I
Patchouly	I	I
Phenyl Ethyl Alcohol	S	I
Rosemary USP	S	S
Sandalwood East Indies	S	S
Terpineol	S	S
Viridine	S	S
Ylang Bourbon	S	I

S = Soluble

C = Cloudy

I = Insoluble

* Data supplied by Givaudan-Delawanna Inc.

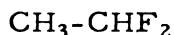
SOLUBILITIES OF "GENETRONS"

The "Genetrons" such as "Genetron" 11, 101, and 320 are excellent solvents for such ketones as acetone, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, diacetone alcohol, and isophorone; for chlorinated solvents such as carbon tetrachloride, methylene chloride, ethylene dichloride, propylene dichloride, perchloroethylene, and trichloroethylene; and for alcohols such as anhydrous ethanol, isopropanol, sec-butyl alcohol, and isobutanol. They are fairly good solvents for esters such as ethyl acetate,

isopropyl acetate, amyl acetate, "Cellosolve" acetate, and n-butyl acetate; and higher alcohols such as n-butyl alcohol and isoamyl alcohol. They are poor solvents for such glycols as propylene, triethylene, ethylene, and diethylene; mineral oils and waxes.

1, 1-DIFLUOROETHANE

"Genetron" 100



Ethylidene Fluoride

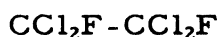
1, 1-Difluoroethane is a colorless liquefied gas, used as a solvent and propellant.

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	-24.7°C (-12.5°F)
Melting point	-117°C (-178.6°F)
Critical temperature	107.5°C (225.5°F)
Flammable limits	3.7-18 vol. % in air
Freezing point	-117°C (179°F)
Heat of vaporization @ B. P.	139.5 Btu/lb 5119 g cal/g mole
Liquid density @ 70°F	56.7 lb/cu ft
@ 130°F	50.9 lb/cu ft
@ 70°F	0.909 g/cu cm
@ 130°F	0.815 g/cu cm
Molecular weight	66.05
Saturated liquid viscosity @ 40°F	0.401 centipoise
@ 70°F	0.243 centipoise
@ 130°F	0.186 centipoise
Solubility of "Genetron" in water @ 70°F	0.32% by wt
Solubility of water in "Genetron" @ 70°F	0.17% by wt
Toxicity	
Estimated grouping via rating system of Underwriters' Labs.	Group 6 (probably)
Vapor pressure @ 70°F	77.22 psia
@ 130°F	191.5 psia

sym- **TETRACHLORODIFLUOROETHANE**

"Freon" BF



"Freon-112"

Commercial grade "Freon" BF (formerly "Freon-112") is a mixture of the symmetrical and unsymmetrical isomers, and may be a water-white liquid or soft white solid depending on purity and room temperature (freezing point 50-70°F). Although this solvent has recently become available on a commercial scale, it has been known for many years, and some of its chemical properties were studied as far back as twenty five years ago. As a typical member of the "Freon"-type compounds, it is offered as another high boiling solvent possessing such characteristics as nonflammability, chemical inertness, and low toxicity. It is miscible with fixed and essential oils, aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, alcohols, phenols. "Freon" BF is either a poor or a non-solvent for most inorganic salts and organic acids. Generally, its solubility behavior is similar to carbon tetrachloride or any completely halogenated compound of low molecular weight. The freezing point can be substantially lowered when small quantities of other solvents are added to tetrachlorodifluoroethane.

PHYSICAL PROPERTIES

Boiling point @1 atm	199.0°F (92.8°C)
Critical pressure	500.0 psia 34 atm.
Critical temperature	532°F (278°C)
Density	
@ 86°F, Liquid	$\left\{ \begin{array}{l} 13.64 \text{ lb/gal} \\ 102.1 \text{ lb/cu ft} \\ 1.634 \text{ g/cc} \end{array} \right.$
@ 199°F, Vapor (sat'd)	$\left\{ \begin{array}{l} 0.438 \text{ lb/cu ft} \\ 7.02 \text{ g/liter} \end{array} \right.$
Diffusivity in air	
@ 77°F (25°C), 1 atm.	$\left\{ \begin{array}{l} 0.065 \text{ sq cm/sec} \\ 0.252 \text{ sq ft/hr} \end{array} \right.$

Freezing point	79°F (26°C)
Latent heat of vaporization @ B. P.	41.0 Btu/lb 22.8 cal/g
Molecular weight	203.8
Refractive index of liquid @ 77°F	1.413
Solubility in water @ saturation pressure, 70°F (21.1°C)	0.013% by wt
Surface tension @ 86°F	23.0 dynes/cm
Viscosity @ 86°F Liquid	1.21 centipoises
Odor	Slightly camphor- like when con- centrated
Vapor pressure @ 21.11°C (70°F)	45 mm Hg

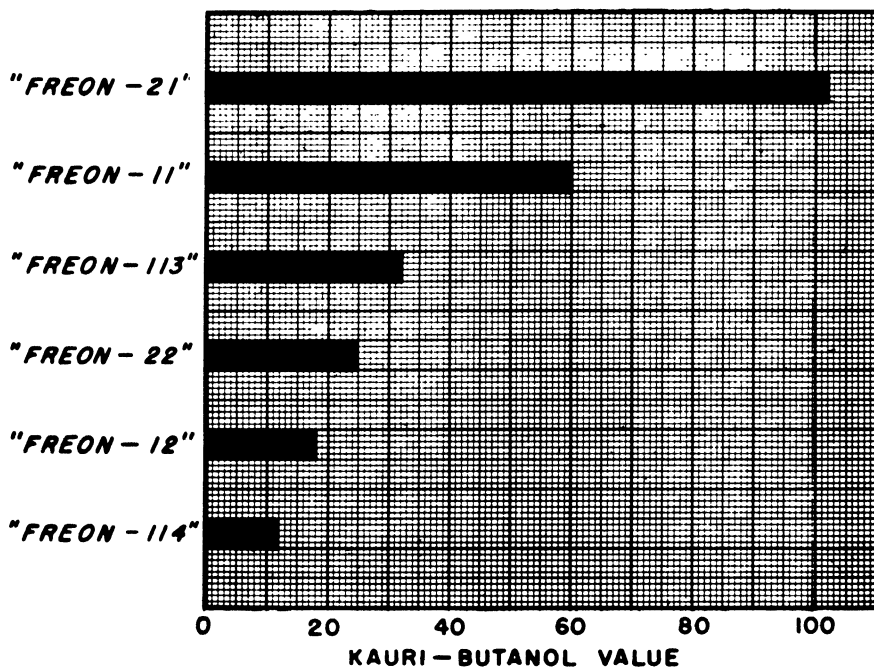
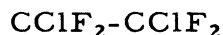


Fig. 1. Kauri-butanol values for the "Freon" compounds at 25°C (77°F)

sym- **DICHLOROTETRAFLUOROETHANE**

"Freon-114"



sym-Dichlorotetrafluoroethane is the least soluble and has the lowest solvent power of any of the commercial "Freon" compounds. Because it has a high ratio of fluorine to chlorine in its molecule, it possesses a high degree of thermal and chemical stability. It is used as a refrigerant.

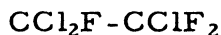
PHYSICAL PROPERTIES

Boiling point @ 760 mm	3.55°C (38.4°F)
Chlorides	None
Color	Clear and water-white
Critical pressure	474 psia
Critical temperature	145.7°C (294.3°F)
High-boiling impurities	Not more than 0.05% by vol.
Flammability	Noncombustible and nonflammable
Melting point	-94°C (-137°F)
Moisture	Not more than 0.0025% by wt
Noncondensable gases	Not more than 5.0% by vol. in vapor phase
Odor	Faint and ethereal

uns- **TRIFLUOROTRICHLOROETHANE**

"Freon-TF"

"Freon-113"



"Genetron 226"

Trifluorotrichloroethane is a water-white liquid, nonflammable and noncombustible, with an ethereal odor similar to carbon tetrachloride. It is an excellent solvent for alcohols, halogenated hydrocarbons, aromatic and aliphatic hydrocarbons, phenols, fixed

and essential oils. Generally, it is a poor solvent for inorganic salts, organic acids, water-soluble gums, and some synthetic resins. At room temperature it is miscible with such liquid organic compounds as: acetone, anisole, benzene, benzyl alcohol, bromoform, α -bromonaphthalene, carbon tetrachloride, castor oil, cetane, chlorobenzene, chloroform, α -chloronaphthalene, citral, clove oil, dichloromethane, ether, ethyl alcohol, ethylene glycol monobutyl ether, n-heptane, n-hexane, iodobenzene, kerosene, methyl alcohol, nitrobenzene, "Perclene," quinaldine, "Triclene," and xylene. It is very soluble with such organic compounds as: azobenzene, benzophenone, camphor, cocoa butter, cottonseed oil, naphthalene, theobromine, thymol, and tribromophenol; moderately soluble with: acetanilide, benzil, benzoic acid, damar, diphenyl, diphenyl carbinol, ester gum, ethyl bromide, hexachloroethane, p-nitrobenzoylacetoacetic ester, phthalic anhydride, and stearic acid; very slightly soluble with: acetamide, "Amberol F7 Light," anthracene, anthranilic acid, antipyrine, gelatin, gum mastic, indigo, iodoform, malic acid, phenol, salicylic acid, succinic acid, "Sulfonal," tartaric acid, "Trional," and urea; and insoluble with: agar, aniline, anthraquinone, "Bakelite SR821," cane sugar, casein, cellulose acetate, dimethylglyoxime, diphenylamine, egg albumen, "Glyptol 1102," glycerol, gum arabic, malonic acid, mandelic acid, methylene blue, methylene iodide, monochloroacetic acid, nitrocellulose ($\frac{1}{2}$ sec.), phenolphthalein, resorcinol, shellac, and thiourea.

Trichlorotrifluoroethane is used as a solvent in molecular weight determinations. It is also a solvent in degreasing electric motors and other equipment without affecting the insulation. It is often used in the formulation of solvent mixtures of low toxicity and low flammability.

PHYSICAL PROPERTIES

Boiling point @1 atm.	117.6°F (47.6°C)
Critical pressure	495.0 psia 33.7 atm.
Critical temperature	417.4°F (214.1°C)
Density @70°F (21.1°C)	
Liquid	$\left\{ \begin{array}{l} 13.14 \text{ lb/gal} \\ 98.26 \text{ lb/cu ft} \\ 1.574 \text{ g/cc} \end{array} \right.$
Vapor (sat'd)	$\left\{ \begin{array}{l} 0.1851 \text{ lb/cu ft} \\ 2.965 \text{ g/liter} \end{array} \right.$
Dielectric constant	
Liquid @86°F (30°C)	2.44
Diffusivity in air @77°F (25°C), 1 atm.	0.068 sq cm/sec 0.264 sq ft/hr
Freezing point	-31.0°F (-35.0°C)
Heat capacity @70°F (21.1°C), Btu/lb/°F or cal/g/°C	
Liquid	0.213
Vapor (sat'd)	0.152
Latent heat of vaporization @B. P.	63.12 Btu/lb 35.07 cal/g
Molecular weight	187.4
Refractive index of liquid @79.7°F (26.5°C)	1.355
Relative dielectric strength @73°F (23°C), 1 atm., (nitrogen = 1)	2.6 (0.4 atm.)
Solubility of water @70°F (21.1°C)	0.009% by wt
Solubility in water @saturation pressure, 70°F (21.1°C)	0.017% by wt
Surface tension @77°F (25°C)	19.0 dynes/cm
Thermal conductivity @70°F (21.1°C), Btu/hr/sq ft/°F/ft	
Liquid	0.0537
Vapor	0.00430
Viscosity @70°F (21.1°C)	
Liquid	0.694 centipoises
Vapor	0.0102 centipoises

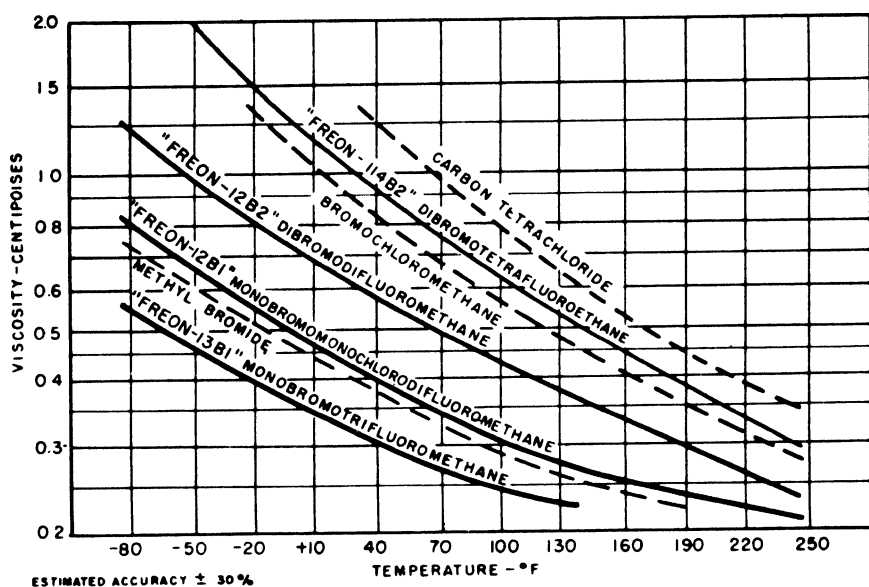
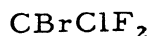


Fig. 2. Estimated liquid viscosity

DIFLUOROBROMOCHLOROMETHANE

"Freon-12B1"



Difluorobromochloromethane is a liquid in which all of the hydrogen atoms have been replaced with fluorine, chlorine, and bromine atoms. It is used as a solvent and as a fire extinguishing agent.

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	-4°C (25°F)
Critical density	0.713 g/cc
Critical pressure	595 psia
Critical temperature	153.8°C (308.8°F)
Freezing point	-160.5°C (-257°F)

Liquid density @ -40°F	2.01 g/cc 16.8 lb/gal
@ 70°F	1.83 g/cc 15.3 lb/gal
@ 130°F	1.70 g/cc 14.2 lb/gal
Loading density	1.68 g/cc
Loading pressure	90 psia
Molecular weight	165.4

DIFLUORODIBROMOMETHANE

"Freon-12B2"

CBr_2F_2

Difluorodibromomethane is a colorless liquid with a very low freezing point. It is both a fluoro and bromo derivative of methane. It is used as a fire extinguishing liquid and as a special solvent.

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	24.5°C (76.1°F)
Critical density	0.844 g/cc
Critical pressure	600 psia
Critical temperature	198.2°C (388.7°F)
Freezing point	-141.6°C (-222.9°F)
Liquid density @ -40°F	2.46 g/cc 20.5 lb/gal
@ 70°F	2.28 g/cc 19.0 lb/gal
@ 130°F	2.15 g/cc 18.0 lb/gal
Loading density	2.13 g/cc
Loading pressure	38 psia
Molecular weight	209.8

TABLE 37
Swelling of Elastomers in Fire Extinguishing Agents.
Maximum Percent Increase in Length at Room Temperatures

	"Freon-12B1"	"Freon-12B2"	"Freon-13B1"	"Freon-114B2"	CH ₂ BrCl
Hycar OR-15	5	11	1	7	49
Perbunan 26	10	23	0	10	50
Neoprene GN-A	13	27	0	6	34
Hypalon E-7	7	29	2	10	40
GR-S	15	24	1	15	26
Natural Rubber	23	34	1	26	32
Butyl	2	47	2	24	15
Thiokol FA	4	8	1	4	*
Silicone 23	15	36	22	33	14

* No measurement possible - test pieces disintegrated.

TABLE 38
Effectiveness of Agents in Extinguishing Standard Gasoline Fires

Common Name	Chemical Formula	Pounds of Agent to Extinguish Standard Fire
Methyl bromide	CH_3Br	0.10
"Freon-13B1"	CBrF_3	0.10
"Freon-12B1"	CBrClF_2	0.105
Bromochloromethane	CH_2BrCl	0.11
"Freon-114B2"	$\text{CBrF}_2\text{-CBrF}_2$	0.12
"Freon-12B2"	CBr_2F_2	0.125

TABLE 39
Effectiveness of Fire Extinguishing Agents in Laboratory Explosion-Prevention Tests

Common Name	Chemical Formula	Effectiveness		Boiling Point	
		Vol. %	Wt. %	$^{\circ}\text{C}$	$^{\circ}\text{F}$
Carbon tetrachloride	CCl_4	2.5	12.7	76.8	170.2
"Freon-13B1"	CBrF_3	1.1	5.6	-60	-76
Bromochloromethane	CH_2BrCl	1.0	4.5	67	152.6
"Freon-114B2"	$\text{CBrF}_2\text{-CBrF}_2$	0.85	7.4	47.5	117.5
Methyl bromide	CH_3Br	0.8	2.7	4.5	40.1
"Freon-12B2"	CBr_2F_2	0.5	3.7	24.5	76.1
"Freon-12B1"	CBrClF_2	0.5	2.9	-4	25

TRIFLUOROMONOBROMOMETHANE

"Freon-13B1" CBrF_3

Trifluoromonobromomethane is a most unusual liquid because of its low freezing point of -270.4°F .

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	$057.8^{\circ}\text{C} (-72.0^{\circ}\text{F})$
Critical density	0.745 g/cc
Critical pressure	575 psia

Critical temperature	67.0°C (152.6°F)
Freezing point	168°C (-270.4°F)
Liquid density @ -40°F	1.912 g/cc 15.95 lb/gal
@ 70°F	1.567 g/cc 13.07 lb/gal
@ 130°F	1.243 g/cc 10.38 lb/gal
Loading density	1.24 g/cc
Loading pressure	450 psia
Molecular weight	148.9

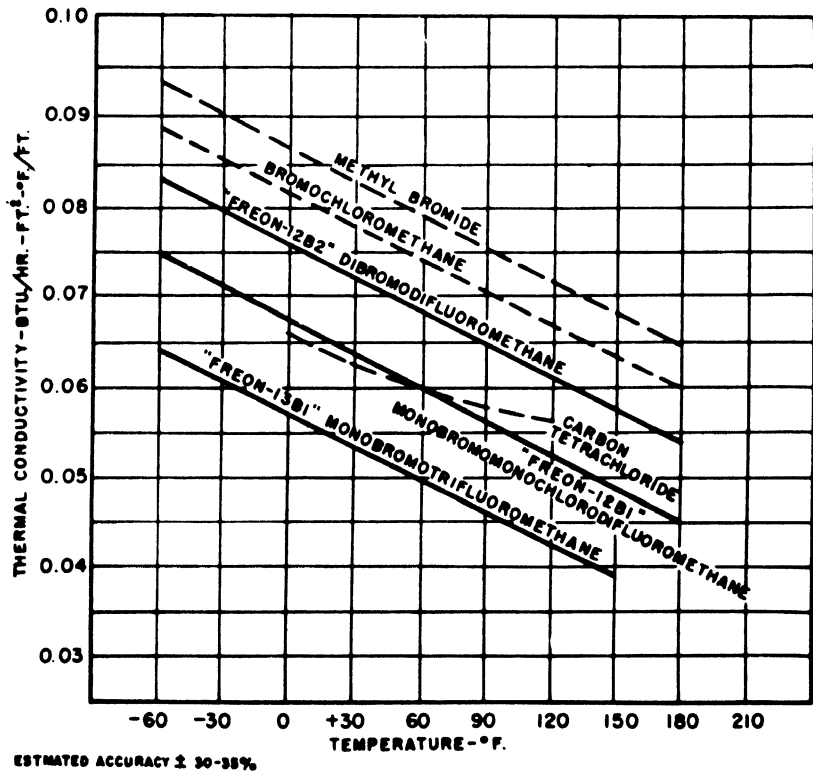


Fig. 3. Estimated thermal conductivity of the liquid.

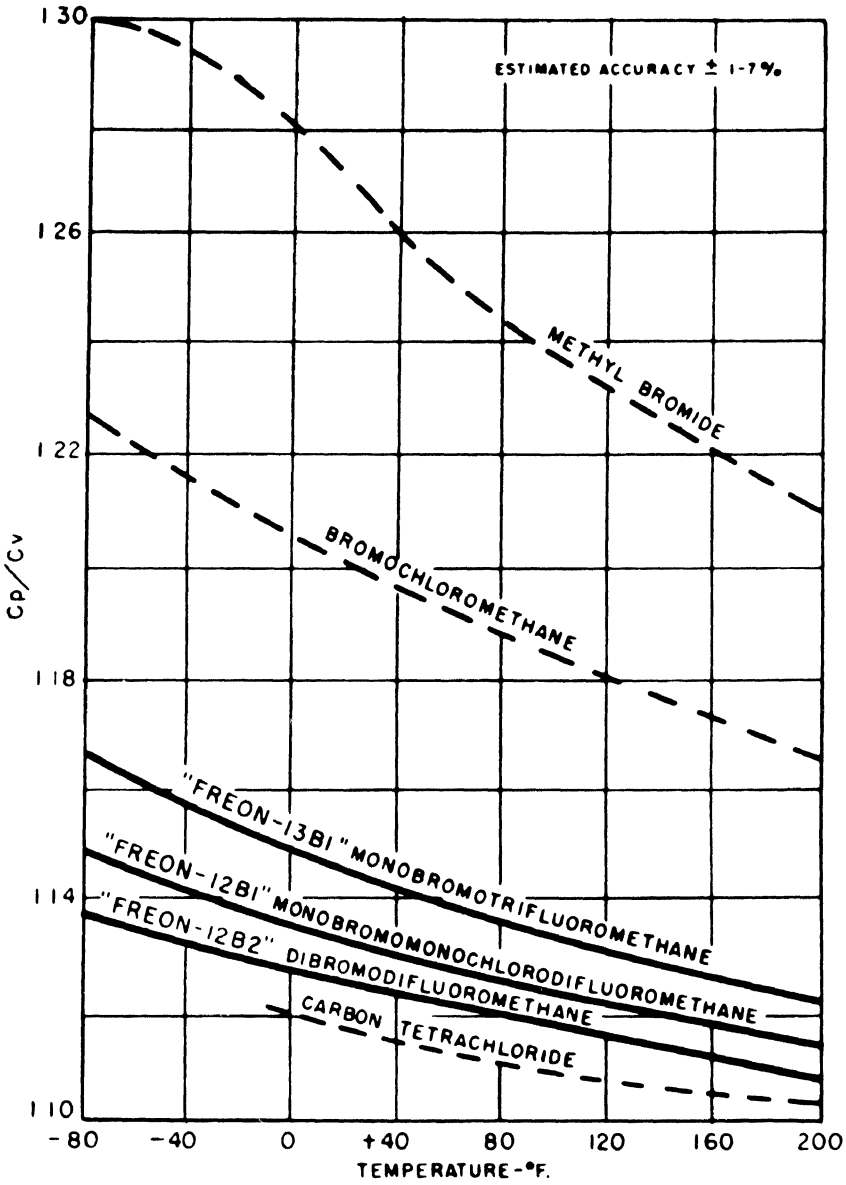


Fig. 4. Ratio of specific heats of the vapor at zero pressure.

TABLE 40

Solubility of "Freon-13B1" in Various Liquids
At Atmospheric Pressure and 25°C (77°F)

Solvent	Weight % "Freon-13B1" in Solution
n-Heptane	6.3
Acetone	4.8
Toluene	4.1
Methanol	3.7
White oil (Ave. M. W. 225)	3.1
Water	0.03

TETRAFLUORODIBROMOETHANE

"Freon-114B2"

$\text{CBrF}_2\text{-CBrF}_2$

PHYSICAL PROPERTIES

Boiling point @ 1 atm.	47.5°C (117.5°F)
Critical density	0.790 g/cc
Critical pressure	510 psia
Critical temperature	214.5°C (418°F)
Freezing point	-110.5°C (-166.8°F)
Liquid density @ -40°F	2.33 g/cc 19.4 lb/gal
@ 70°F	2.16 g/cc 18.0 lb/gal
@ 130°F	2.05 g/cc 17.1 lb/gal
Loading density	2.04 g/cc
Loading pressure	18.5 psia
Molecular weight	259.9

TABLE 41
Effect of Liquid Fire Extinguishing Agents on
Various Materials at Room Temperature

Material	Percent Change in Volume of Material Caused by Various Agents				
	CBrF_3 + Water	CBr_2F_2	CBr_2F_2 + Water	CH_2BrCl	CH_2BrCl + Water
Neoprene	0	25	37	50	50
Buna N	0	11	11	40	40
Hycar	0	0	0	60	60
Polyethylene	0	11	0	0	0
Saran	0	0	0	0	0
Vynlite	0	-12	-12	**	**
Tygon	0	-8	-8	**	**
Silastic	0+	0+	0+	12	12

** Formed gel.

TABLE 42
Heat of Vaporization of Fire Extinguishing Agents

Common Name	Chemical Formula	Boiling Point °C	Latent Heat of Vaporization at the Boiling Point	
			Cal/g mol	Cal/g
"Freon-12B1"	CBrClF_2	-4	5300	32.0
"Freon-12B2"	CBr_2F_2	24.5	6100	29.1
"Freon-13B1"	CBrF_3	-57.8	3940	26.5
"Freon-114B2"	$\text{CBrF}_2\text{-CBrF}_2$	47.5	6400	25
Methyl bromide	CH_3Br	3.6	5715	60.1
Carbon dioxide	CO_2	...	2750 ¹	62.5 ¹
Carbon tetrachloride	CCl_4	76.8	7138	46.4

¹ Data at -10°C since CO_2 has no liquid state at atmospheric pressure.

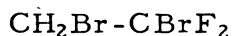
TABLE 43

Toxicity of Vapors from Extinguishing Agents Used on Gasoline Fires

Agent	Percent Mortality in 14 Days	
	Mice	Rats
No Agent	0	0
No Fire		
"Freon-13B1"	0	0
"Freon-12B2"	5	0
Carbon tetrachloride	5	0
Bromochloromethane	0	5
Rapid Extinction of Fire		
"Freon-13B1"	0	6
"Freon-12B2"	80	15
Carbon tetrachloride	5	10
Bromochloromethane	0	3
Slow Extinction of Fire		
"Freon-13B1"	0	0
	5	3
	37	0
"Freon-12B2"	100	9
	10	33
Carbon tetrachloride	10	33
	20	8
Bromochloromethane	32	29

DIBROMODIFLUOROETHANE

"Genetron" B-111



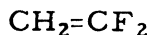
This water-white, very dense liquid is a solvent for special processes. It also exhibits flame-extinguishing ability.

PHYSICAL PROPERTIES

Boiling point	93.4°C (200.1°F)
Liquid density @20°C (68°F)	2.224 g/cc 18.6 lb/gal
Melting point	-63.1°C (-81.6°F)
Molecular weight	223.87
Nonflammable	Extinguishes fire
Vapor pressure @21.11°C (70°F)	45.8 mm Hg

DIFLUOROETHYLENE

Vinylidene fluoride



"Genetron" 150

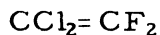
Difluoroethylene is a colorless gas having a faint ethereal odor. It is used as a special solvent and in synthesis.

PHYSICAL PROPERTIES

Boiling point	-82°C (-121°F)
Critical density	0.417 g/cc
Critical pressure	643 psia
Critical temperature	30.1°C (86.2°F)
Melting point	144°C (-227.2°F)
Molecular weight	64.04
Specific gravity @0°C	0.815
Vapor pressure @21.11°C (70°F)	534 psia

DICHLORODIFLUOROETHYLENE

"Genetron" 170



Dichlorodifluoroethylene is a nonflammable, colorless gas having a faint ethereal odor. Its major use is in synthesis.

PHYSICAL PROPERTIES

Boiling point	19.0°C (66.2°F)
Critical density	0.52 g/cc
Critical pressure	570 psia
Critical temperature	186°C (303°F)
Melting point	-115°C (-175°F)
Molecular weight	132.93
Specific gravity @20°C	1.4385
Vapor pressure @21.11°C (70°F)	15.9 psia

TABLE 44
COMPARATIVE REFRIGERANT CHARACTERISTICS OF **genetrons**
and Other Basic Refrigerants

(PERFORMANCE BASED ON 5°F EVAPORATOR TEMPERATURE AND 86°F CONDENSER TEMPERATURE)

	genetron 11	genetron 12	genetron 141	genetron 226	Carrene 7	Methyl Chloride	Ammonia	Sulfur Dioxide
Chemical Formulae	CCl ₃ F	CCl ₂ F ₂	CHClF ₂	C ₂ Cl ₃ F ₃	Note 1	CH ₂ Cl	NH ₃	SO ₂
Molecular Weight	137.4	120.9	86.5	187.4	99.3	50.5	17.0	64.1
Boiling Pt. (°F) at 1 Atmosphere Pressure	74.7	-21.6	-41.4	117.6	-28.0	-10.8	-28.0	14.0
Evaporator Pressure at 5°F (p.s.i.g.)	24.0*	11.8	28.3	27.9*	16.4	6.5	19.6	5.9*
Condensing Pressure at 86°F (p.s.i.g.)	3.6	93.2	159.8	13.9*	113.4	80.0	154.5	51.8
Freezing Point (°F) at 1 Atmosphere Pressure	-168	-252	-256	-31	-254	-144	-108	-104
Critical Temperature (°F)	388	233	205	417	221	289	271	315
Critical Pressure (p.s.i. absolute)	635	582	716	495	631	969	1657	1142
Compressor Discharge Temperature (°F)	112	100	131	86	105	172	210	191
Compression Ratio (86°F/5°F)	6.24	4.07	4.06	8.02	4.12	4.48	4.94	5.63
Saturated Liquid Viscosity at 5°F (centipoises)	0.650	0.328	0.286	1.200	—	0.293	0.250	0.503
Saturated Liquid Viscosity at 86°F (centipoises)	0.405	0.251	0.229	0.619	—	0.234	0.207	0.281
Vapor Viscosity at 5°F & 1 Atmosphere Pressure (centipoises)	0.0096	0.0114	0.0114	0.0093†	—	0.0095	0.0085	0.0111
Vapor Viscosity at 86°F & 1 Atmosphere Pressure (centipoises)	0.0111	0.0127	0.0131	0.0105†	—	0.0109	0.0102	0.0131
Saturated Liquid Density at 5°F (lbs./cu.ft.)	97.88	90.00	83.34	103.20	80.11	61.65	41.11	92.00
Saturated Liquid Density at 86°F (lbs./cu.ft.)	91.38	80.63	73.36	96.96	71.23	56.24	37.16	84.44
Saturated Vapor Density at 5°F (lbs./cu.ft.)	0.0815	0.6735	0.8034	0.0370	0.657	0.2237	0.1227	0.1558
Saturated Vapor Density at 86°F (lbs./cu.ft.)	0.4461	2.569	3.213	0.2569	2.598	0.9253	0.5643	0.8440
Specific Volume of Saturated Vapor at 5°F (cu.ft./lb.)	12.27	1.49	1.25	27.04	1.52	4.47	8.15	6.42
Latent Heat of Vaporization at 5°F (B.t.u./lb.)	84.0	69.5	93.6	70.6	—	180.7	565.0	169.4

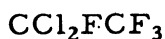
Net Refrig. Effect of Liquid (86°F/5°F) (B.t.u./lb.)	67.5	51.1	69.3	53.7	61.1	150.2	474.4	141.4
Specific Heat of Liquid at 86°F (B.t.u./lb. °F)	0.21	0.24	0.34	0.22	—	0.39	1.14	0.39
Specific Heat of Vapor at Constant Pressure of 1 Atmosphere & 86°F (B.t.u./lb. °F)	0.13	0.15	0.15	0.15	—	0.24	0.51	0.15
Specific Heat Ratio at 86°F & 1 Atm. ($k=C_p/C_v$)	1.14	1.14	1.18	1.09	—	1.20	1.32	1.29
Coefficient of Performance	5.09	4.70	4.66	4.92	4.61	4.90	4.76	4.87
Horsepower/Ton Refrigeration	0.927	1.002	1.011	0.960	1.022	0.962	0.989	0.968
Refrigerant Circulated/Ton Refrig. (lbs./min.)	2.96	3.92	2.89	3.73	3.27	1.33	0.422	1.41
Liquid Circulated/Ton Refrig. (cu.in./min.)	56.0	83.9	68.0	66.5	79.3	40.9	19.6	28.9
Compressor Displacement/Ton Refrig. (c.f.m.)	36.32	5.81	3.60	100.76	4.97	5.95	3.44	9.09
Thermal Conductivity of Saturated Liquid at 32°F (B.t.u./ft. ² /hr. °F)	0.0680	0.0559	0.0704	0.0576	—	0.103	0.29	0.122
Thermal Conductivity of Saturated Liquid at 86°F (B.t.u./ft. ² /hr. °F)	0.0609	0.0492	0.0595	0.0521	—	0.089	0.29	0.111
Thermal Conductivity of Vapor at 32°F & 1 Atm. Pressure (B.t.u./ft. ² /hr. °F)	0.0045	0.0048	0.0060	0.0038†	—	0.0053	0.0128	0.0050
Thermal Conductivity of Vapor at 86°F & 1 Atm. Pressure (B.t.u./ft. ² /hr. °F)	0.0048	0.0056	0.0068	0.0045†	—	0.0065	0.0145	0.0056
Stability (Toxic Decomposition Products)	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes
Toxicity (Underwriters' Laboratories Group No.)	5A	6	5A	4-5	5A	4	2	1
Flammability	None	None	None	None	None	Yes	Yes	None
Relative Dielectric Strength of Vapor (compared with Ethyl Chloride as Unity)	3.00	2.40	1.31	2.60	—	1.06	0.82	1.90
Odor	Ethereal	Ethereal	Ethereal	Ethereal	Ether.	Ether.	Acrid	Acrid
Type of Compressor in Which Usually Used	Cen.	All	Rec-Rot	Cen.	Rec-Rot	All	All	Rec.
Evaporator Temperature Range, °F	-20 to 50	-100 to 50	-125 to 50	-25 to 50	-100 to 50	-80 to 50	-90 to 20	-60 to 50
Water Sol. in Liq. Refrig. at 32°F (gms./100 gms. Refrig.)	0.0036	0.0026	0.060	0.0036	—	0.026 at -10°F	High	High
Water Sol. in Liq. Refrig. at 86°F (gms./100 gms. Refrig.)	0.013	0.012	0.15	0.013	—	—	High	High
Oil Solubility (Miscibility With Lubricating Oils)	Yes	Yes	Partial	Yes	Yes	Yes	No	No

Note 1. "Carrene" 7 is an azeotropic mixture of "Genetron" 100(CH_3CHF_2) and "Genetron" 12(CCl_2F_2)

* Inches of mercury vacuum † At 0.1 atmosphere ‡ At 0.5 atmosphere

uns-DICHLOROTETRAFLUOROETHANE

"Genetron" 320



Dichlorotetrafluoroethane is a colorless, non-flammable gas with a faint ethereal odor. It is used as an aerosol propellant, and is more frequently used in combination with "Genetron" 12 in products which contain water. Other aerosol products use a combination of this solvent with "Genetron" 101. Other uses are as a refrigerant and for charging special thermometers.

PHYSICAL PROPERTIES

Boiling point @ 1 atm. press.	37.4°F (3.1°C)
Freezing point @ 1 atm. press.	ca. -76°F (ca. -60°C)
Heat of vaporization @ B.P.	60.46 Btu/lb (5396 g cal/g mole)
Liquid density @ 70°F	92.2 lb/cu ft (1.477 g/cu cm)
Molecular weight	170.93
Vapor pressure @ 70°F	28.07 psia
@ 130°F	75.20 psia
Flammable limits	Nonflammable
Saturated liquid viscosity	
@ 70°F	0.458 centipoise
@ 130°F	0.347 centipoise
Solubility of "Genetron" in water	
@ 70°F	0.01% by wt
Solubility of water in "Genetron"	0.006% by wt
Toxicity	
Estimated grouping via rating system of Underwriters' Labs.	Group 6 (probably)

TRIFLUOROCHLOROETHYLENE

"Genetron" 265

 $\text{CClF}=\text{CF}_2$

Trifluorochloroethylene is a nonflammable, colorless gas with a faintly ethereal odor. Its major use is in the preparation of its polymers (thermoplastics) and low-molecular weight greases, oils, and waxes. It is also a chemical intermediate.

PHYSICAL PROPERTIES

Boiling point	-27.9°C (-18.2°F)
Critical density	0.55 g/cc
Critical pressure	585 psia
Critical temperature	106.7°C (224.1°F)
Melting point	-157.5°C (-251.5°F)
Molecular weight	116.48
Specific gravity @20°C	1.315
Vapor pressure @21.11°C (70°F)	83 psia

HEPTACOSAFLUOROTRIBUTYLAMINE

Fluorochemical N-43 (31)

 $(\text{C}_4\text{F}_9)_3\text{N}$

This colorless, inert liquid is made by replacing all the hydrogen of tributylamine with fluorine. It is a good solvent for other fluorinated liquids but is found to be a poor solvent for most other materials. As a stable liquid, it resists the action of reducing and oxidizing agents. Also, because of its extreme stability, low power factor, low dielectric and high dielectric strength, it makes a good liquid dielectric. It is also used as a selective solvent.

PHYSICAL PROPERTIES

Boiling point	177°C (351°F)
Coefficient of vol. expansion per °C	
25-40°C, 77-104°F	1.2×10^{-3}
140-160°C, 284-320°F	2.1×10^{-3}
Density @25°C, 77°F	1.872 g/cc
Formula weight	671
Freezing point (Glass Point)	-66°C (-87°F)
Heat of vaporization @ B. P.	11,100 cal/mole 16.5 cal/g
Odor	Odorless
Pour point	-50°C (-58°F)
Refractive index @25°C, 77°F	1.2910
Specific heat @25-40°C, 77-104°F	0.27 cal/g/°C
Surface tension @25°C, 77°F	16.1 dynes/cm
Vapor pressure @ 25°C, 77°F	0.3 mm Hg
Viscosity @25°C, 77°F	2.74 centistokes

FLUOROCHEMICAL O-75

This colorless liquid is a completely fluorinated cyclic ether with the empirical formula $C_8F_{16}O$. It is believed to be a five- or six-membered ring having a fluorinated side chain, with the oxygen atom in the ring. It is a good solvent for other fluorinated materials but a poor one for most other materials. It is extremely stable and inert and therefore makes a good dielectric and heat transfer liquid. It should make an unusual selective solvent (44).

PHYSICAL PROPERTIES

Boiling point	101°C (214°F)
Coefficient of vol. expansion per °C	
25-40°C, 77-104°F	1.6×10^{-3}
40-80°C, 104-176°F	2.0×10^{-3}
Density @25°C, 77°F	1.760 g/cc

Formula weight	416
Freezing point	-100°C (-148°F)
Heat of vaporization @ B.P.	8,700 cal/mole 20.9 cal/g
Odor	Odorless
Pour point	-100°C (-148°F)
Refractive index @25°C, 77°F	1.276
Specific heat @25-40°C, 77-104°F	0.26 cal/g/°C
Surface tension @25°C, 77°F	15.2 dynes/cm
Viscosity @25°C, 77°F	0.82 centistoke

1, 1, 1-TRIFLUOROETHANOL

Trifluoroethanol

$\text{CF}_3\text{CH}_2\text{OH}$

Trifluoroethanol is a colorless and stable liquid with an agreeable odor. It is miscible with polar solvents but immiscible with most nonpolar organic solvents. It is used as a specialized solvent and is soluble in water, ethyl alcohol, acetone, ethyl acetate, benzene, toluene, and ethylene dichloride. Carbon tetrachloride, n-hexane and cyclohexane are only slightly soluble, while carbon disulfide, n-heptane and methyl cyclohexane are insoluble.

PHYSICAL PROPERTIES

Acidity as acetic acid	0.25% max.
Boiling range	72-75°C
Boiling point	74.05°C
Clarity	Clear
Fire point	108°F
Flash point (O. C.)	90°F
Freezing point	-43.5°C
Heat of vaporization (calc'd)	97.1 g cal/g 9710 g cal/mole

Moisture content	2.0% max.
Refractive index, n_D^{25}	1.2910-1.2880
Specific gravity, 22/25°C	1.387 ± 0.003 g/ml
Surface tension, 32.5°C	20.6 dynes/cm
Viscosity @ 20°C	1.996 centipoises
@ 60°C	0.796 centipoise

TABLE 45

Properties of Some Derivatives and Products Related to Trifluoroethanol (45)

Compound	Formula	B. P. (°C)	M. P. (°C)	Density
Trifluoroacetic acid	$\text{CF}_3\text{CO}_2\text{H}$	71	-15.6	1.4820
Bis(trifluoroethyl) ether	$(\text{CF}_3\text{CH}_2)_2\text{O}$	63	...	1.3667
Trifluoroethyl vinyl ether	$\text{CF}_3\text{CH}_2\text{OCH}=\text{CH}_2$	42	...	
Trifluoroethyl methyl ether	$\text{CF}_3\text{CH}_2\text{OCH}_3$	30-32	...	1.1661(3°C)
Trifluoroethyl chloride	$\text{CF}_3\text{CH}_2\text{Cl}$	6.1	...	1.389 (0°C)
Trifluoroethyl bromide	$\text{CF}_3\text{CH}_2\text{Br}$	26.3 ¹	-93.9 ¹	1.7881 ¹
Trifluoroethyl iodide	$\text{CF}_3\text{CH}_2\text{I}$	55	...	2.142 ¹
Trifluoroethyl benzoate	$\text{CF}_3\text{CH}_2\text{OOC}_6\text{H}_5$	184	...	
Trifluoroethyl sulfite	$(\text{CF}_3\text{CH}_2\text{O})_2\text{SO}$	74/80 mm	...	
Trifluoroethyl maleate	$(\text{CF}_3\text{CH}_2\text{OCOCH})_2$	110/33 mm	...	
Trifluoroethyl fumarate	$(\text{CF}_3\text{CH}_2\text{OCOCH})_2$	...	39.5	
Trifluoroethyl succinate	$(\text{CF}_3\text{CH}_2\text{O}_2\text{CCH}_2)_2$	101/40 mm	...	
Bis(trifluoroethyl) sulfide	$(\text{CF}_3\text{CH}_2)_2\text{S}$	83	...	1.25
Trifluoroethyl mercaptan	$\text{CF}_3\text{CH}_2\text{SH}$	38	...	
Trifluoroethyl nitrite	$\text{CF}_3\text{CH}_2\text{ONO}$	15.8	...	
Trifluoroethyl nitrate	$\text{CF}_3\text{CH}_2\text{ONO}_2$	66.0-66.5 ¹	...	1.4958
Tetrakis (trifluoroethyl) silicate	$(\text{CF}_3\text{CH}_2\text{O})_4\text{Si}$	60-61/25 mm	...	
Trifluoroacetonitrile	CF_3CN	-63.9	...	
Trifluoroacetamide	CF_3CONH_2	162.5	75	
Trifluoroacetaldehydol	$\text{CF}_3\text{CH}(\text{OH})_2$	103-105	68-70	1.468 ¹
Trifluoroacetal	$\text{CF}_3\text{CH}(\text{OC}_2\text{H}_5)_2$	113	...	
1,1,1-Trifluoro-2,2,2-trichloroethane	CF_3CCl_3	46	14.2	1.5790
1,1,1-Trifluoro-2-chloro-2-bromoethane	CF_3CHClBr	50-50.5	-60	1.862

¹ Literature value.

Section III
CHLORINATED HYDROCARBONS

CHLORINE

Chlorine is the second member of the halogen group. Next to fluorine it is the most electronegative element consisting of two isotopes, Cl^{35} and Cl^{37} . Its atomic number 17 refers to the 17 negatively charged electrons in the outer shell of the chlorine atom, which balance the number of positively charged protons in the nucleus. Being mono-, tri-, penta- and heptavalent, it forms the following series of compounds:

- 1 Chlorides	Cl^-	e. g.	NaCl
+ 1 Hypochlorites	ClO^-	e. g.	NaOCl
+ 3 Chlorites	ClO_2^-	e. g.	NaClO_2
+ 5 Chlorates	ClO_3^-	e. g.	NaClO_3
+ 7 Perchlorates	ClO_4^-	e. g.	NaClO_4

Chlorine, either as a gas or liquid, is nonflammable and nonexplosive with air, but will support combustion and sometimes explode with certain other compounds. Either gaseous or liquid chlorine does not attack such metals as copper, iron, lead or steel at ordinary temperatures when in a dry state. Moist chlorine is very corrosive to all common metals except gold, platinum, and silver. Tantalum at temperatures below 150°C (302°F) is totally inert to both moist and dry chlorine. Good resistance to chlorine is also shown by special high silica iron alloys, "Monel," and "Hastelloy." Moist chlorine at low pressures is often handled in equipment made of earthenware, glass, or porcelain.

Since chlorine has a strong affinity for other substances, it reacts with most of the elements and with many inorganic and organic compounds, usually with the evolution of heat. For this reason, chlorine is never found free in nature. It usually occurs as sodium chloride (common salt) found in oceans, salt lakes, salt wells, and beds of salt rock. It is also

found in combination with other elements such as carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) and sylvite (potassium chloride).

The versatility of the chlorine element is demonstrated with striking clarity when its presence is observed in other compounds. The great chemical inertness which it has the power to impart is shown in such products as chlorinated rubber, chlorinated paraffin, flame-resistant materials, weatherproofed fabrics, extenders and plasticizers in vinyl resin compounds, and additives for extreme-pressure lubricants. On the other hand, as a reactive intermediate, chlorine serves to increase the reactivity of other compounds. One such example is the insecticide isobornyl thiocynoacetate made from the reaction of monochloroacetic acid with pine terpenes yielding esters having a very reactive chlorine atom. Because this chlorine atom can easily be replaced by a thiocyno group, the insecticidal properties which this group imparts, are thus attained. In compounds where chlorine is actually present in the final molecule, it contributes its own unique properties. As in toxaphene, chlorinated camphene, an insecticide made from pine terpenes and chlorine, the presence of the chlorine in the molecule adds stability and some of its own toxicity.

Chlorinated hydrocarbons exhibit valuable chlorine properties that distinguish them as solvents. These compounds are stable, nonflammable, have low water solubility, and are excellent solvents for fats, waxes, oils, and grease. Examples of such compounds are methylene chloride, chloroform, carbon tetrachloride, trichloroethylene, and perchloroethylene, etc. They are easily recovered from extracted residues by simple distillation. They are good non-polar solvents for hydrocarbons, alkaloids, and rubber, but their solvent action is only limited on highly polar derivatives such as sugars, proteins, inorganic acids, and glycerol. An active solvent mixture is obtained by adding a small amount of ethyl alcohol to chlorinated hydrocarbons. Chlorinated solvents having narrow boiling ranges and low boiling points are employed successfully as extractants.

Early in the eighteenth century, when the bleaching effect of chlorine was first applied commercially to textiles and paper pulp, new chemical directions were initiated which foreshadowed our present high standard of living. The multiplicity of materials that came into being through chlorination created refinements which have become a part of our daily lives. Today, chlorine and its compounds enter into the preparation of products in so many essential fields of usefulness that they have become almost indispensable for the continued progress of our civilization.

The early history of chlorine is of particular interest because it played so prominent a part in scientific investigation that led to the shaping of modern chemistry. Its final discovery as an element involved the rejection of old chemical theories and the introduction of new ones based on sounder chemical facts. Geber, the Arabian alchemist of the eighth century, having discovered aqua regia and nitrohydrochloric acid, was very likely aware of chlorine as the highly disagreeable-smelling, very corrosive, greenish-yellow fumes driven off when heated. Since aqua regia became the indispensable solvent for the extraction of gold from its ore, the belief seems well supported that other alchemists knew of its existence as chlorine fumes.

The eighteenth century is noted for the number of brilliant investigations that contributed to the rapidly growing importance of chemical science. The discovery of chlorine was made conclusively by Scheele in 1774 while heating manganese dioxide with muriatic acid. From his accurate description of the properties of the fumes, we recognize them as belonging to chlorine. He observed that this greenish-yellow gas with a very pungent odor, very corrosive and irritating to the respiratory organs, and soluble in water, had a lasting bleaching effect on materials such as paper, vegetables, and flowers, and also noticed its action on metals and metal oxides.

Being an ardent believer in the phlogiston theory, Scheele named this gas "dephlogisticated muriatic acid." The phlogistic theory, which until then had been of prime importance in chemical theory, attempted to explain the phenomena of combustion, oxidation, and reduction. The term "phlogiston" which Scheele thought chlorine to be, comes from the Greek word meaning "flame," thus explaining its designation as the flammable principle thought to be given off during any combustion process.

The theory of phlogiston lost ground and was finally upset with the development of the chemistry of gases. In their separate investigations of the composition of air, Priestley, in 1772, collected chlorine gas over mercury and named it "marine acid air," while Lavoisier in 1789 named it "oxymuriatic acid," both holding the view that chlorine was muriatic acid to which oxygen had been added. Thus, within the period between 1774 and 1810, Scheele's gas occupied the attention of such chemists as Lavoisier, Berthollet, Gay-Lussac, Berzelius, Thenard, and finally Humphrey Davy whose investigations between 1808 and 1810 proved conclusively that this gas, heretofore thought to be an oxygenated muriatic acid, was in fact an elementary body and its presence in muriatic acid was in combination with hydrogen.

The first practical application of the bleaching properties of chlorine was made by Berthollet in 1785 who prepared Scheele's gas by heating a mixture of salt, manganese dioxide, and vitriol and then dissolving the chlorine in water. Working at a chemical plant situated in Quai de Javelle in Paris, he improved this bleach by adding the chlorine to a solution of caustic potash. This product is still known there as "Eau de Javelle." This process was later brought to Scotland in 1798 by the chemist James Watt to be manufactured by Charles Tennant. Chlorinated milk of lime was also manufactured and a further improvement was made in 1799 by producing a dry bleaching product, chlorinated hydrate of lime, which could be transported with greater ease and safety.

In 1888 Knietsch made it possible to produce chlorine on a commercial scale by the cooling and compression of the gas, using a suitable apparatus which would resist its corrosive action. Berthollet's method of preparing chlorine continued to be used until 1868 when Deacon and Hurter in 1868 patented an improved method called the "Deacon" process, in which hydrochloric acid was decomposed with oxygen.

Davy had shown considerable interest early in the nineteenth century in the decomposing action of an electric current, and was the first to discover that solutions of alkaline chlorides were decomposed by an electric current, to yield chlorine. Faraday, who extended the application of electricity to chemical procedures, discovered in 1833 and formulated the laws that control the action of an electric current in aqueous salt solutions. The electrolytic method of preparing chlorine commercially was first applied by a German company in 1890. The first American plant to prepare commercial chlorine electrolytically was at Rumford Falls, Maine, in 1893, using Le Sueur diaphragm cells.

At best, such production remained on a small scale because no practical dynamo for electric current had as yet been devised. The introduction of the Gramme dynamo-electric machine in 1872 supplied cheap mechanically-produced electric energy, and the commercial development of chlorine got under way. By 1909, the American chlorine industry had grown to tank-car shipments and it continued to increase with the need for paper and textile bleaches.

To achieve this phenomenal growth of chlorine production, continuous research was carried on to develop cells having larger capacity, lower voltage, higher current efficiency, higher caustic concentration, and requiring less space to accommodate them. From this concerted effort we have today the Gibbs and Vorce round cells, Allen-Moore and Nelson narrow rectangular cells, and the more recent Hooker Electrochemical almost cubical cell. Other large

manufacturers have developed diaphragm cells of their own. Two notable cell designs—the deposited diaphragm cell developed during 1925-1929, and the basic Hooker type "S," developed during 1929-1930—contributed their share to chlorine production. Today, the capacity of Hooker diaphragm cells is so large that they employ up to 24,000 amperes.

At present, two fundamental types of processes are in operation for the manufacture of chlorine, namely, electrolytic processes and chemical processes. The electrolytic processes are carried out by diaphragm cells, mercury cells, or fused salt cells, whereas the chemical methods include the nitrosyl process and a modified Deacon process which involves the catalytic air oxidation of hydrogen chloride. Chlorine production by chemical means is relatively unimportant at present since it accounts for only 1 per cent of chlorine production in the United States. The electrolytic processes include the electrolysis of molten sodium chloride by the Downs process which is primarily used in the manufacture of elemental sodium, and the electrolysis of brine by the Nelson and Vorce processes.

The mercury cells have been used largely in European chlor-alkali production because mercury was comparatively cheap, asbestos could only be obtained by importation from America, and nickel for evaporators was short in supply. Mercury cells have also had a history of use and development in the United States. As early as the mid-1890's, Castner's mercury cell patents and graphitization of carbon anodes were put into operation on a pilot-plant scale by the Mathieson Chemical Corporation. Later, in 1897, these cells were used in full production in a plant built to produce 30 tons of chlorine per day. After World War I, this process was discontinued because the small capacity of the rocking cell made it impractical for large-scale production. Improvements were made with the object of developing a stationary cell of larger capacity, where the circulation of mercury to and from the electrolyzer could be

accomplished by a separate pump rather than by the rocking motion of the cell. In 1947, a Mathieson E-4 cell was introduced, and in 1951 the newer Mathieson's E-8 cells were put in operation.

The caustic-chlorine plant at Muscle Shoals, Alabama, was the first large installation of DeNora mercury cells in this country constructed to provide chlorine for defense purposes. About 150 tons of chlorine is the estimated daily output from the 30,000-ampere DeNora cells. Monsanto Chemical Company has made an agreement for the use and sale of the DeNora Amalgam cell in the United States and in some other countries. These cells were first developed by Impianti Elettrochimici of Milan, the company of Dr. Oranzio DeNora, and in 1936 the first unit of the DeNora cells was built in Italy.

The cell is a long, narrow steel trough lined with stone resistant to chemicals. Blocks of dense graphite suspended in the trough serve as anodes. Hard rubber covers seal the top of the trough making it gas-tight. The cathode is a thin film of mercury which flows by gravity along the bottom of the trough. The graphite anodes are placed 0.2 inch from the cathode. As the brine flows over the mercury it is decomposed by the electric current passing between the mercury and the graphite electrodes. Chlorine is released and the sodium forms a mercury amalgam upon solution in the mercury.

Diaphragm and mercury cells are the two leading sources of chlorine production in the United States. The diaphragm cells produce by far the greater portion of chlorine, amounting to about 79 per cent of the total output. This cell is distinctly different from the mercury cell in that a porous asbestos diaphragm separates the graphite anodes from the perforated steel cathode. During electrolysis, saturated salt brine flows continuously from the anodes, through the diaphragm, and through the cathode. This steady flow of brine and the diaphragm of asbestos prevent backward diffusion of the sodium hydroxide and reaction with chlorine at the anodes. In mercury cells,

chlorine is liberated at the anode during electrolysis, and a sodium amalgam is produced at the cathode. Both processes produce chlorine, sodium hydroxide, and hydrogen but in the mercury cell process, another step is required to separate the caustic soda and hydrogen from the amalgam. This is carried out in a separate decomposer compartment.

To conserve space and facilitate its use, chlorine gas is dried and then liquefied by compression and cooling to a low temperature. During this process, noncondensable gases are removed and the liquid chlorine is loaded in steel containers.

Chlorine contributed to the development of our modern chemical industry in providing the means of producing white paper and fabrics, in the treatment of sewage, to provide potable water, and in the production of germicides, disinfectants, and anesthetics. Today, this basic chemical is essential in the formation of a multiplicity of products among which are solvents, extractants, plastics, synthetic rubbers, non-toxic refrigerants, high-test gasolines, dyes, insecticides, herbicides, vitamins, sulfa drugs, and many other chemicals. To appreciate the prodigious growth of the chlorine industry, thirty years ago the production of chlorine amounted to 550 tons per day. Today, 11,000 tons are produced daily with increasing demand from such industries as automotive fluids, plastics and resins, insecticides and herbicides, refrigerants, and repellents. It is predicted that the demand for chlorine will increase 50 per cent by 1960.

Before World War I, the chemical industry in the United States was restricted to the manufacture of simple inorganic chemicals. This situation was caused by Germany's world monopoly of the more complex organic chemicals among which were dyes, perfumes, and medicinals. These synthetic coal tar products included in their production the chlorination of coal tar crudes to form intermediates from which the final products were made. During World War I, with the blockade of German commerce by the Allies,

dyes and medicinals were no longer obtainable and American industry was faced with the necessity of producing her own complex organic materials. In 1915 the first monochlorobenzol plant was built which led to the development of other organic chemicals including explosives desperately needed for the war effort. After World War I, chlorine's unique properties were more intensively investigated giving place to the extraordinary increase in the production of synthetic chlorinated organic compounds indispensable now as solvents, insecticides, and intermediates.

The earliest example of the preparation of chlorohydrocarbons took place in 1795 when the Dutch chemists Delman, Bondt, van Teroostrwyk, and Lauwerenburgh prepared ethylene dichloride claiming it to be a new "oil." After 1920, rapid development of chlorinated hydrocarbons was largely due to the availability of the lower paraffins, the cheapness of chlorine, the ease with which chloro-organic compounds could be prepared, and their ready conversion to other derivatives. In 1922 the chlorination of a paraffin in the C 20 range was produced on a semi-commercial scale to form an unsaturated drying oil as a substitute for linseed oil. Early attempts were made to chlorinate petroleum in order to obtain chlorinated intermediates, fatty acids, esters, isoprene, etc. In the early 1930's, chlorinated paraffins were produced on a commercial scale for use as "pour point" depressants and as oil additives.

The 1930's also witnessed the development of chlorinated rubber, first in Germany and later in the United States. Its early use was as a film former in the paint industry. But with the approach of World War II, chlorinated rubber and paraffin products were in great demand for flameproofing textiles, tenting, camouflage nets, and the production of flame-retardant paints. The 1930's also produced synthetics that were often superior and always cheaper than the substances they were intended to replace.

Somewhat later, extreme pressure lubricant additives were developed for the automotive industry, as well as agricultural chemicals and synthetic rubber modifiers.

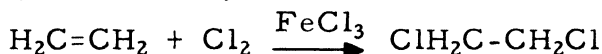
The chlorination of the saturated and unsaturated lower paraffins has produced compounds of great economic importance. By 1950, the United States production of chlorinated paraffins and olefins was about 1.8 billion pounds. Although these compounds are used as general solvents, cleaning fluids, refrigerants, anesthetics, etc., they are also largely used as the raw materials for synthesis of a large number of compounds such as alcohols, alkylene oxides, ethers, amines, hydrocarbons, alkaryl compounds, etc. Of the paraffin hydrocarbons, only methane and the pentanes are chlorinated to a considerable extent.

Commercial chlorination is accomplished by (1) liquid-phase photochemical, which leads to polychloro compounds, (2) gas-phase photochemical, and (3) gas-phase thermal. Complete reaction of the chlorine is possible with the latter method and a high yield of monochloro compounds (90-95%) is produced when the mole ratio of hydrogen to chlorine is about 5:1 or more. Except for chloromethanes, the monochloro compounds are the most desirable.

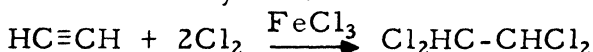
Either liquid- or gas-photochemical chlorination is carried out at a relatively low temperature using mercury arc lamps to provide the light energy required. The costs are high so that these processes have a more limited commercial application than the gas-phase thermal chlorination, particularly for paraffin hydrocarbons.

Thermal chlorination is carried out under temperatures above 250 to 300°C for the dissociation of chlorine which occurs to an appreciable extent in this temperature range. The heat of the chlorine reaction is utilized in preheating the reactants. The high reaction temperature is favorable for rapid reaction and high reactor capacities, and the specific heat of the excess hydrocarbon controls the reaction.

The mechanism of chlorination is dependent upon the type of organic compound involved, the specific chlorinating agent used, and the presence of an appropriate catalyst or chlorine carrier. Thus, in an addition reaction, a reaction occurring with unsaturated compounds to form saturated compounds, the chlorine enters the organic molecule without displacing any other element:

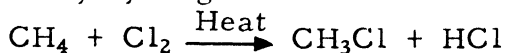


This reaction is demonstrated by any organic compound having one carbon-to-carbon double bond to which two atoms of chlorine will attach themselves. By this reaction ethylene dichloride (1,2-dichloroethane) is formed where ethylene containing one double bond adds two atoms of chlorine. Another example is acetylene tetrachloride (1,1,2,2-tetrachloroethane) formed by the addition of four chlorine atoms to the triple bond of acetylene.



In an addition reaction with aromatic compounds such as benzene, 3 moles of halogen saturates the aromatic ring with the activation of ultraviolet radiation.

The reaction employed most frequently in industrial applications involves the substitution of another element, usually hydrogen.



This reaction is utilized to a large extent with paraffin and aromatic hydrocarbons because of the ease with which it proceeds under reasonably mild conditions. Examples of this reaction with aliphatic hydrocarbons are observed when methyl chloride, methylene chloride, chloroform, or carbon tetrachloride is produced from methane. The quantity of chlorine added to the methane will determine the formation of these compounds. Other examples are ethyl chloride produced by the chlorination of butane and amyl chlorides made by the chlorination of pentane. Because

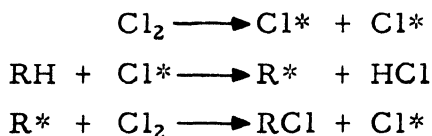
of the ease of reaction by substitution where light or heat initiates the reaction, a catalyst is usually not required.

The substitution reaction with aromatic hydrocarbons such as benzene, toluene, xylene, etc., involves either the chlorination of the nucleus or ring, or the side chains or alkyl groups attached to the ring. Either substitution reaction can be accomplished, depending on the method used.

The chlorination of the nucleus or ring requires the presence of a catalyst or halogen carrier such as iron or iron chloride the chlorides of antimony, molybdenum, aluminum, phosphorus, sulfur and iodine which are able to exist in two valences as chlorine compounds. In the presence of these substances, the reaction will occur at relatively low temperatures.

The chlorination of the side chain or alkyl group is the same as the chlorination of an aliphatic hydrocarbon where ultraviolet radiation activates or catalyzes the reaction. It is necessary to avoid the presence of iron.

On closer examination of the reaction mechanism involved in the chlorination of a paraffin hydrocarbon or the side chain of an alkyl benzene, it is assumed that the initial formation of chlorine atoms occurs by dissociation of chlorine molecules. These atoms then react with the hydrocarbon to form both a hydrochloride and a free radical. A free radical is any atom or group possessing an unpaired electron. The free radical then proceeds to react with another molecule of chlorine to give both the desired monochloride and a chlorine atom which continues the reaction chain.

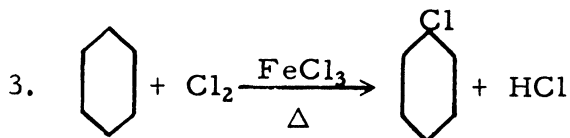
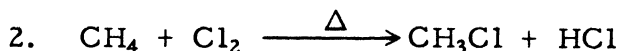
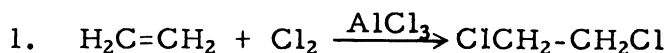


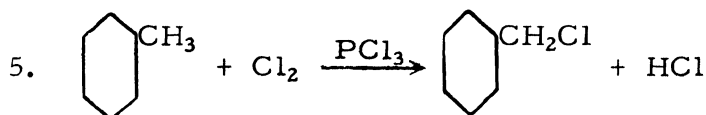
To cause the dissociation of chlorine, either thermal or photochemical energy is required. When impurities are present, the chains are stopped since these substances react preferentially with the active chain carriers. Products from toluene chlorinated in this manner are benzyl chloride, benzal chloride, and benzotrichloride.

Chlorine reacts with organic compounds other than the hydrocarbons. One such reaction involves oxidation, as in the preparation of chloral where chlorine reacts with alcohol, oxidizing the hydroxyl group to the aldehyde group. Another chlorination requires that the carboxyl group contained in the compound should not enter the reaction, as in the case of acetic acid which can be chlorinated to either mono-, di-, or trichloroacetic acid. Nitro compounds, sulfonic acids, esters, and ethers utilize a similar type of chlorination reaction. A third such chlorination requires the protection of certain groups from chlorine attack, as represented by the important amino compounds.

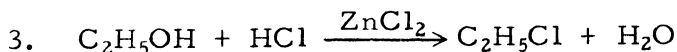
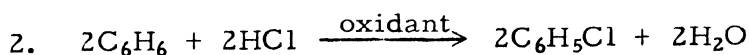
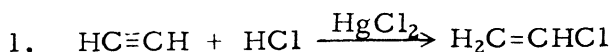
The processes which demonstrate some of these chlorine reactions are as follows:

A. Chlorination by chlorine and a catalyst:





B. Chlorination by hydrochloric acid and a catalyst:



C. Chlorination by sodium hypochlorite in an alkaline medium.

D. Chlorination by phosgene (COCl_2).

E. Chlorination by sulfuryl chloride (SO_2Cl_2).

Some of the specific chemicals used to introduce chlorine into organic and inorganic compounds are: chlorine (Cl_2), sulfur monochloride (S_2Cl_2) or sulfur dichloride (SCl_2), sulfuryl chloride (SO_2Cl_2), thionyl chloride (SOCl_2), hydrogen chloride (HCl), and phosgene (carbonyl chloride, COCl_2).

Since sulfur monochloride and sulfur dichloride are so closely related, their uses are often considered together. These substances react with unsaturated hydrocarbons to introduce sulfur or chlorine, or both, into the molecule. Unsaturated fatty acids will react with sulfur chlorides to produce polymerized products. Ethylene oxide and propylene oxides will react with sulfur chlorides to form chloro derivatives. As chlorinating agents, sulfur chlorides serve as a ready source of chlorine with the additional advantage of safer handling and storage.

Sulfuryl chloride is an inorganic compound used principally for the introduction of chlorine into the molecule. The advantages of using sulfuryl chloride

as the chlorinating agent are: (1) far less heat of chlorination is produced than when elemental chlorine is used; (2) selective chlorination is made possible when catalysts are reacted under closely controlled conditions at different temperatures with different proportions of reactants. The best known chlorination reaction involves sulfuryl chloride and sodium salts of organic acid, which form organic acid chlorides. A specific reaction involving sodium acetate and sulfuryl chloride, yields acetyl chloride; another, involving sulfuryl chloride, yields chlorinated phenol and its derivatives. meta-Cresol will react with sulfuryl chloride to form p-chloro-meta-cresol. Aniline, an aromatic amine, is readily chlorinated to form mono-, di-, and trichloro derivatives. By using aluminum chloride as a catalyst, benzene and toluene can be chlorinated.

The sulfuryl chloride reaction is similar to the photochemical reaction of gaseous chlorine. This is explained by the following generalizations: (1) Substitution of hydrogen on a secondary carbon atom is considered to take place in preference to substitution on a primary carbon atom. (2) It is found that a second substituent chlorine atom tends to attach itself to the aliphatic chain, as far as possible from the first chlorine atom. (3) It is further observed that substitution of a second chlorine atom upon a carbon atom already bearing a halogen substituent is difficult, and a third chlorine atom cannot be attached to one carbon atom in this way.

Derivatives and homologs of toluene undergo side-chain chlorination when organic peroxides are used as catalysts. Other peroxide-catalyzed reactions include the chlorination of alkenes by which saturated dichloro derivatives result.

Thionyl chloride (SOCl_2) is an inorganic chemical chlorinating agent. Its usefulness rests on the fact that it can replace a hydroxyl group in acids, alcohols, and phenols. When used with organic acids, either acid chlorides or anhydrides are formed.

Hydrogen chloride is an anhydrous gas which reacts with such alcohols as methyl and ethyl to form methyl and ethyl chlorides. Ethers may be used in place of alcohols and such reactions result in the formation of alkyl chlorides. Alkyl chlorides can also be obtained by adding hydrogen chloride to unsaturated aliphatic hydrocarbons. An outstanding procedure is the one in which vinyl chloride is formed by the action of hydrogen chloride upon acetylene. Hydrogen chloride will also react with organic acid anhydrides to form the corresponding acid chlorides.

Phosgene, (carbonyl chloride, COCl_2) is an acid chloride of carbonic acid and may be considered an organic compound. Alcohols react with phosgene to form chlorformates or carbonates. Examples of these are the methyl, ethyl, propyl, isobutyl, and isoamyl chlorformates. When an excess of alcohol is present, a symmetrical disubstituted ester of carbonic acid is produced. An example of this is the formation of dimethyl carbonate. The reaction between phenols and phosgene is less violent although the end products are the same. Amines react with phosgene to form chloramides, substituted ureas, or isocyanates. Olefins, aluminum chloride, and phosgene will react to form alpha-chlor acid chlorides. Organic acids react with phosgene to yield acid chlorides and anhydrides.

When chlorine gas is passed through benzene in the presence of gamma-radiation from a Co^{60} source, a violent reaction takes place in which chlorine combines with the benzene by the process of addition. As a result of this reaction the solid material formed is a mixture of stereoisomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. When toluene is chlorinated by this method, chlorine enters both the ring and the side chain. The results of the analyses are given in Tables 46 and 47.

TABLE 46
Analyses of Some Samples of Benzene Hexachloride (33)

Approx. Reaction Temp., °C	Benzene, Vol. %	CCl ₄ (solvent), Vol. %	Gamma Isomer in Benzene Hexa- chloride, %
20	10	90	11.3†
20	20	80	12.5
-10	10	90	12.3
-10	30	70	12.8

* From infrared analysis.

† Overchlorinated.

TABLE 47
Summary of Three Reaction Runs of Toluene and Chlorine in the 10-Kilocurie Co⁶⁰ Gamma Source (33)

Volume of sample, ml	Control temp., °C	Total radiation time, min.	Gamma flux rate, kiloreps/hr (est. av.)	Total dose received, kiloreps in air	Weight of hexachloro addition product produced, g	Over-all yield, %	Amount of product produced, moles	Moles/liter- kilorep (av.)	Av. value of G for addition
1400	20	71	24	28	185	4.5	0.61	0.014	14,000
1450	20	121	22	44	371	8.8	1.2	0.017	18,000
1500	20	226	22	82	778	18	2.5	0.018	19,000

TABLE 48
Summary of Chlorination Experiments¹ (37)

Hydrocarbon	Temp., °C	Hydro- carbon	Reactants Cl ₂ ²	Chlorinating agent SO ₂ Cl ₂ ³	Mole % chlorin- ation	Products Alkyl chlorides	t- Chloride
Cumene	25.0 ± 0.1	0.60	0.034		5.7	0.0312	0.0236
Cumene	25.0 ± .1	.70	.056		9.3	.0542	.0403
Cumene	80.0 ± .1	.87	.050		5.7	.0465	.0310
Cumene	80.0 ± .1	.71	.043		6.0	.0430	.0298
2, 3-Dimethylbutane	25.0 ± .1	.90	.044		4.9	.0469	.0173
2, 3-Dimethylbutane	25.0 ± .1	.88	.048		5.4	.0482	.0183
2, 3-Dimethylbutane	55.0 ± 2	1.05		0.140	13.3	.1324	.0679
Triptane	-15.0 ± 0.2	0.90	.049		5.3	.0508	.0113
Triptane	-15.0 ± 0.2	.85	.045		5.3	.0518	.0123
Triptane	0.0 ± 2	1.17	.130		11.1	.1250	.0409
Triptane	0 ± 0.5	1.00	.030		3.0	.0283	.0092
Triptane	25.0 ± .1	0.71	.026		3.4	.0257	.00455
Triptane	25.0 ± .1	.70	.021		3.1	.0213	.0037
Triptane	80.0 ± .1	.53	.031		5.8	.0342	.0062
Triptane	80 ± 2	1.02		.070	14.6	.0695	.1131
Triptane ⁴	80 ± 2	1.23		.120	10.3	.0228	.0341
Isobutane	-15.0 ± 0.5	1.5	.115		7.8	.1173	.0389
Isobutane	-15.0 ± 0.5	1.5	.111		7.4	.1043	.0341
2, 3, 4-Trimethylbutane	25.0 ± 0.1	0.13	.011		8.3	.0093	.00365

¹ All quantities in moles.

² ± 0.003 mole.

³ 1% by wt benzoyl peroxide.

⁴ Sulfuryl chloride added dropwise over reaction period.

⁵ Analysis of the hydrolysis data indicated the presence of 0.0012 mole of a tertiary chloride which hydrolyzed rapidly (presumably 3-chloro-2, 3, 4-trimethylpentane) and 0.0024 mole of a slower solvolyzing tertiary chloride (presumably 2-chloro-2, 3, 4-trimethylpentane).

TABLE 49
Directive Effects in Aliphatic Chlorination (35)

Compound	Reaction	Group	Isomer Distribution, %		
			1-(α -)	2-(β -)	3-(γ -) 4-
n-Propylbenzene	SO ₂ Cl ₂ , ~80°	C ₆ H ₅ -	50		
n-Butane	Cl ₂	CH ₃ -	40	40	20
1-Chlorobutane	SO ₂ Cl ₂ , ~80°	ClCH ₂ -	24	51	25
n-Propyl acetate	SO ₂ Cl ₂ , ~80°	CH ₃ CO ₂	25	46	29
	Cl ₂ , liq., ~80°		23	42	35
	Cl ₂ , gas, 101.5°		0	69	31
1,1-Dichlorobutane	SO ₂ Cl ₂ , ~80°	Cl ₂ CH-	13	49	38
n-Propylsilicon trichloride	SO ₂ Cl ₂ , ~80°	Cl ₃ Si-	13	46	41
n-Butyric acid	SO ₂ Cl ₂ , ~80°	HO ₂ C-	10	45	45
1,1,1-Trichlorobutane	SO ₂ Cl ₂ , ~80°	Cl ₃ C-	8	42	50
1-Chlorobutane	SO ₂ Cl ₂ , ~80°	Cl-	7	22	47
n-Butyl chloride	SO ₂ Cl ₂ , 80°	ClOC-	3	49	48
	Cl ₂ , gas, 101.5°		5	65	30
	Cl ₂ , liq., r. t.		20	60	20
	Cl ₂		3	50	47
n-Propyl trichloroacetate	SO ₂ Cl ₂ , ~80°	Cl ₂ =	2	13	48
1,1-Dichlorobutane	SO ₂ Cl ₂ , ~80°	Cl ₃ ≡	..	8	42
1,1,1-Trichlorobutane	Cl ₂ , liq., 16°	F ₃ C-	0	45	55
1,1,1-Trifluorobutane	Cl ₂ , liq., 16°	F ₃ ≡	..	0	45
1,1,1-Trifluorobutane					55

TABLE 50
Physical Properties of Intermediates and Products (35)

Compound	B. P., °C., corr.	Press., mm.	Density d_{25}^{25}	Refractive Index, n_D^{25}	Chlorine, % ¹ Found Calcd.
1-Chlorobutane	77.5-78.5	745		1.3995	
1,1-Dichlorobutane	114.8-115.1	752	1.0797	1.4305	
1,2-Dichlorobutane	122.9-123.3	743	1.1118	1.4425	
1,3-Dichlorobutane	133.0-133.2	744	1.1083	1.4414	
1,4-Dichlorobutane	154.1-154.2	749	1.1324	1.4522	
1,1,1-Trichlorobutane	133.1-133.3	750	1.2242	1.4483	65.88
1,1,2-Trichlorobutane	156.3-156.8	746	1.2787	1.4667	65.88
1,1,3-Trichlorobutane	153.2-153.8	750	1.2514	1.4593	65.88
1,1,4-Trichlorobutane	183.6-183.8	754	1.2967	1.4753	65.88
1,1,1,2-Tetrachlorobutane	69.1-69.4	20.0	1.3952	1.4812	72.39
1,1,1,3-Tetrachlorobutane	69.5-69.8	20.0	1.3747	1.4772	72.39
1,1,1,4-Tetrachlorobutane	86.8-87.1	20.0	1.4001	1.4858	72.39
1,1-Dichloro-1-butene	103.3-103.5	747		1.4465	56.74
α -Chlorobutyraldehyde	106-108 ³	740		1.441	35.38
n-Butyryl chloride	101-101.5 ³	745		1.4098	
α -Chlorobutyryl chloride	51.5-51.7	40.0		1.4410	
β -Chlorobutyryl chloride	53.0-53.3	20.0		1.4477	
γ -Chlorobutyryl chloride	71.0-71.2	20.0		1.4597	
Ethyl α -chlorobutyrate	64.2-64.4 ³	20.0		1.4202	
Ethyl β -chlorobutyrate	69.9-70.1 ³	20.0		1.4222	
n-Propyl acetate	101-102	745		1.3823	
1-Chloropropyl acetate	48.6-48.8	20.0		1.4143	
2-Chloropropyl acetate	57.1-57.6	20.0		1.4205	
3-Chloropropyl acetate	58.4-58.8	10.0		1.4275	
n-Propyl chloroacetate	52.6-52.8	10.0		1.4233	

¹ Chlorine analysis by reaction with sodium diphenyl in dimethyl "Cellosolve" [L. M. Liggett, Anal. Chem., 26, 748(1954)].

² Av. of three analyses (56.17, 56.22 and 56.25%).

³ Uncorrected.

The directive effects in aliphatic substitution have been summarized by Ash and Brown (34) with particular emphasis on liquid-phase chlorination reactions. "Twelve groups were arranged in the order of their decreasing activating effect on adjacent carbon atoms: C_6H_5- > CH_3- > $H-$ > CH_3COO- and CH_2Cl- > $CHCl_2-$ and $SiCl_3-$ > $HOOC-$ > $Cl-$ > $COCl-$ > Cl_3CCOO- > CCl_3- > CF_3- . This series has been discussed from a theoretical standpoint under the following headings: Certain aspects of liquid-phase chlorination reactions, the role played by the inductive effect, the 'vicinal effect,' and free radical stability in the chlorination reaction." In this study of the effect of substitution in directing the free radical-atom chlorination, the groups are arranged to indicate the order of influence on the directive effects in aliphatic chlorination: C_6H_5- > CH_3- > $H-$ > $ClCH_2-$ > CH_3COO- > Cl_2CH- > Cl_3Si- > $HOOC-$ > Cl_3C- > $ClOC-$ > $Cl_2=$ > $Cl_3\equiv$ > F_3C- > $F_3\equiv$.

In the sulfonyl chloride chlorination of the 1-chlorobutanes, Russell and Brown come to the conclusion that the acetoxy group is similar to the $ClCH_2C-$ group in directing chlorination (36, 37).

A summary of the kinetics of chlorination is presented below:

"(1) The rate of substitution chlorination of hydrogens on unsaturated carbons is greater than the rate of substitution of hydrogens on unsaturated carbon atoms.

"(2) The rate of substitution chlorination of hydrogens on saturated carbons is greater than the rate of addition chlorination to double bonds at high temperatures; the reverse is true at low temperatures.

"(3) The rate of addition chlorination on double bonds is greater than the rate of substitution of hydrogens on unsaturated carbons.

"(4) The rate of substitution of hydrogens 'alpha' to a chlorine is about the same as the normal rate of substitution of hydrogens on the type of carbon atom concerned.

"(5) The rate of substitution of hydrogens 'beta' to a chlorine is markedly less than the normal rate of substitution of hydrogens on the type of carbon atom concerned.

"(6) The rate of substitution of hydrogens 'gamma' to a chlorine is only slightly less than the normal rate of substitution of hydrogens on the type of carbon atom concerned. For hydrogen 'omega' and farther removed from a chlorine, the rate of substitution is the normal one." (38)

Studying the competitive halogenation of cyclohexane and aralkyl hydrocarbons, Russell and Brown arrive at the following conclusions: "From the reactivities of the alkyl benzenes, it appears that the selectivity of removal of a hydrogen atom is in the order: Chlorine atom, methyl radical, trichloromethyl radical, styrene polymer radical. The bond energies of hydrogen chloride, methane, chloroform and toluene decrease in the same order. Thus, there appears to be a direct correlation between the strength of the new bond being formed and the reactivity of the attacking species. The stronger the new bond, the more reactive the attacking species (chlorine atom, methyl radical, trichloromethyl radical, styrene polymer radical), and the lower its selectivity."

Table 51 shows the relative reactivity of cyclohexane and toluene to photochlorination. From this investigation it is indicated that toluene is 60 times more reactive toward the bromine atom than is cyclohexane. On the other hand, cyclohexane is 11 times more reactive than toluene toward the chlorine atom.

The data in Table 52 are the result of the direct determination made of the heat of substitutive chlorination ($R-H + Cl_2 \rightarrow R-Cl + HCl$) for benzene, chlorobenzene, toluene, cyclohexane, n-hexane, ethylene dichloride, and chloroform.

TABLE 51
The Competitive Halogenation of Cyclohexane and Toluene¹ (39)

Temp., °C	80	80	80	80	80	80	80	80	55	0-2
Reactants										
Cyclohexane	1.486	1.925	0.855	0.789	0.604	0.340			0.325	0.237
Toluene	0.536	1.940	2.610	2.423	1.845	1.068			1.115	1.145
Sulfuryl chloride ²		0.52	0.29							
Chlorine				0.29	0.18	0.12			0.10	0.10
Bromine	0.19									
Products										
Hydrogen chloride										
Alkyl halides	0.190	0.497	0.286	0.285	0.174	0.113			0.096	0.086
Benzyl halide	.179	.040	.060	.068	.043	.027			.105	.112
Halocyclohexane ³	.011	.457	.226	.217	.131	.087			.022	.0318
Cyclohexane ⁴	1.383	1.361	.625	.570	.443	.239			.232	
Toluene ⁴	0.320	1.857	2.548	2.354	1.790	1.038			1.090	
Mole % halogenation	9.4	13.9	8.3	8.9	7.1	8.6			6.9	7.3
Mean cyclohexane-toluene ratio	3.55	0.863	0.287	0.280	0.288	0.275			0.251	
Reactivity of cyclohexane ⁵	0.017	13.2	13.1	11.4	10.6	11.7			15.0	

¹All quantities in moles.

²1% by weight of benzoyl peroxide added

³By difference

⁴Initial quantity minus amount substituted and amount vaporized.

⁵Reactivity of toluene assumed to be 1.00.

TABLE 52

Heats of Substitutive Chlorination (40)

Run No.	R·H(liq.) + Cl ₂ (gas) → R·Cl(liq.) + HCl(gas) at 25°									
	Total HCl liberated, moles	Temp. rise (corr.) °C	Length of main-period min.	Heat evolved (uncorr.) J	Corrections		Heat evolved (corr.) J	Heat of reaction (-ΔH)		
					Evaporation of reactant (add) J	Solution of HCl (deduct) J		kJ/ mole	kg.-cal./ mole	
Benzene → chlorobenzene										
1	0.1432	1.795	23	20,113	(360)*	(1802)*	18,671	130.4	31.2	
2	0.1641	2.020	21	23,098	(420)*	(1302)*	21,716	132.3	31.6	
3	0.1738	2.103	22	23,843	(450)*	(1802)*	22,941	129.5	31.0	
4	0.1735	2.240	23	25,627	491	1635	24,483	141.1	33.7	
5	0.1782	2.227	24	25,684	420	1945	24,159	135.6	32.4	
6	0.1807	2.237	24	25,628	472	1825	24,275	134.3	32.1	
								Mean	32.0	
Chlorobenzene → dichlorobenzenes										
1	0.1661	1.865	28	21,519	97	995	20,621	124.1	29.7	
Toluene → chlorotoluenes (o- and p-)										
1	0.1794	2.303	24	26,281	156	1567	24,870	138.6	33.1	
2	0.1838	2.271	23	26,053	169	1437	24,785	134.9	32.2	
3	0.1641	2.270	25	24,970	130	1557	23,544	143.5	34.3	
4	0.1687	2.253	25	24,715	134	1568	23,281	138.0	33.0	
								Mean	33.2	
Toluene → benzyl chloride										
1	0.1602	2.102	23.5	23,677	124	1611	22,190	138.5	33.1	
2	0.1502	1.980	23.5	21,992	102	1663	20,431	136.0	32.5	
								Mean	32.8	

<i>cyclo</i> Hexane $\longrightarrow$ chloro <i>cyclo</i> hexane									
†1	0.1821	2.244	28	25,507	786	326	25,967	142.6	34.1
†2	0.1832	2.303	26	25,430	822	322	25,930	141.5	33.8
3	0.1748	2.227	22	24,818	766	328	25,256	144.5	34.5
4	0.1779	2.265	24	25,126	771	348	25,549	141.7	34.3
								Mean	34.2
<i>n</i> -Hexane $\longrightarrow$ monochloro- <i>n</i> -hexanes									
†1	0.1794	2.187	27	24,058	1326	258	25,126	140.0	33.5
2	0.1880	2.272	23	24,894	1364	256	26,002	138.3	33.1
3	0.1764	2.143	23	23,701	1297	258	24,740	140.3	33.5
								Mean	33.4
Ethylene dichloride $\longrightarrow$ 1 : 1 : 2-trichloroethane									
1	0.1993	2.231	41	24,824	441	2164	23,122	115.8	27.7
2	0.1757	1.929	37	21,570	382	1431	20,521	116.8	27.9
								Mean	27.8
Chloroform $\longrightarrow$ carbon tetrachloride									
1	0.1470	1.228	25	13,648	1279	630	14,297	97.3	23.3
2	0.2270	1.660	38	18,605	2199	662	20,142	88.7	21.2
								Mean	22.3

* For these earlier runs with benzene the procedure of using two absorber trains was not used. The correction given for evaporation of reactant was based on consideration of Runs 4-6 and the total hydrogen chloride evolved in the run concerned. The correction for the heat of solution of hydrogen chloride was in each case the average of those for Runs 4-6.

† In these particular runs with *cyclo*hexane and *n*-hexane, light was admitted to the calorimeter only for the main-period of the reaction run. The temperature rises have been corrected by an amount based on a subsidiary test of the heat received from the lamp.

Many of the new synthetic coating materials are more difficult to remove or strip because of their resistance. In the early part of this century, most of the paint and varnish removers consisted of benzene, acetone, ethyl acetate, and ethanol. But to meet the greater resistance of paint and varnish, the chlorinated solvents have been receiving increased attention as solvents for this purpose.

The relative stripping efficiencies of various chlorinated solvents were studied and found to be in the following order of descending activity: methylene chloride, chloroform, ethylene dichloride, trichloroethylene, monochlorobenzene, carbon tetrachloride, 1,2,3-trichloropropane, propylene dichloride, ortho-dichlorobenzene, 1,2,4-trichlorobenzene, perchloroethylene and methyl chloroform.

System C-1 (Chlorinated Rubber). The efficiency of methylene chloride was greatly improved by minor and massive additions of methanol and acetone, and by minor additions of "Cellosolve" and dimethylformamide.

System C-2 (Styrene-Butadiene). Since methylene chloride alone showed extreme rapidity of action in this system, no attempt was made to explore the effect of additives.

System D-1 ("Epon"). Methylene chloride stripped this coating within 40 seconds, in view of which it was not considered necessary to test the effect of additives.

System D-2 (Styrenated Alkyd). When 5 per cent of methanol was added to methylene chloride improved removal was observed. The wrinkling time was reduced effectively from no removal after 10 minutes to removal within 60 seconds. The performance was not as good when methyl acetate, benzol, and dimethylformamide were added.

System D-3 (Drying Oils). Methylene chloride by itself showed a wrinkling time of 26 seconds so that there was no need to add to its solvent action.

TABLE 53
Relative Stripping Efficiencies of Chlorinated
Solvents in Standard Paint Remover (41)

Solvent		(Methylene chloride = 100%) Rating
Methylene chloride	(CH ₂ Cl ₂)	100 (45 seconds)
Chloroform	(CHCl ₃)	69
Ethylene dichloride	(CH ₂ Cl-CH ₂ Cl)	45
Trichloroethylene	(CHCl-CCl ₂)	43
Monochlorobenzene	(C ₆ H ₅ Cl)	34
Carbon tetrachloride	(CCl ₄)	22
1, 2, 3-Trichloropropane	(CH ₂ Cl-CHCl-CH ₂ Cl)	17
Propylene dichloride	(CH ₃ -CHCl-CH ₂ Cl)	15
ortho-Dichlorobenzene	(C ₆ H ₄ Cl ₂)	13
1, 2, 4-Trichlorobenzene	(C ₆ H ₃ Cl ₃)	10
Perchloroethylene	(Cl ₂ C=CCl ₂)	7
Methyl chloroform	(CH ₃ =CCl ₃)	0 (no effect in 4 hrs.)

TABLE 54
Wrinkling Time of Binary Solutions Compared to
Methylene Chloride on Water-Based Paints (41)

Co-solvent	% by Vol. Added	(Time in minutes)	(Time in sec.)	
		System A-1 (Polyvinyl Acetate)	System A-2 (Acrylic)	System A-3 (Styrene- Butadiene)
Methylene Chloride	100	15 1/2	129	122
Methanol	5	17	118	122
Methanol	40	21*	189*	138
Methylacetate	5	21	135	101
Methylacetate	40	25*	165*	181*
Acetone	5	18*	140	138
Acetone	40	25*	270*	570*
"Cellosolve"	5	25*	150	119
"Cellosolve"	40	25*	240*	...
Benzol	5	25*	129*	113
Benzol	40	25*	225*	...
Mineral Spirits	5	20*	150*	195*
Mineral Spirits	40	25*	270*	...
Chloroform	5	25*	120	154
Chloroform	40	25	146	...
Dimethylformamide	5	25*	120	...
Dimethylformamide	40	25*	270	...

* Incomplete Removal of Film.

TABLE 55
Wrinkling Time of Binary Solutions Compared to Methylene Chloride on Lacquers (41)
(Time in Seconds)

Co-solvent	% by Vol. Added	System E-1 (Nitrocellulose)	System E-2 (Vinyl)	System E-3 (Vinyl) (200°F.-20 min.)	System E-4 (Cellulose Acetate- Butyrate)
Methylene Chloride	100	NR	110	50	NR
Methanol	5	NR	89	..	NR
Methanol	40	SR	NR	..	NR
Methylacetate	5	NR	90	..	NR
Methylacetate	40	SR	NR	..	NR
Acetone	5	NR	75	..	NR
Acetone	40	SR	105	..	NR
Cellosolve	5	NR	130	..	NR
Cellosolve	40	SR	NR	..	NR
Benzol	5	NR	133	..	NR
Benzol	40	NR	450*	..	NR
Mineral Spirits	5	NR	300*	..	NR
Mineral Spirits	40	NR	NR	..	NR
Chloroform	5	NR	132	..	NR
Chloroform	40	NR	155	..	NR
Dimethylformamide	5	SR	123*	..	NR
Dimethylformamide	40	SR	107	..	NR

NR - No removal after 10 mins.

SR - Slight removal after 10 mins.

System D-4 (Phenolic Resin). At 5 per cent concentration, methanol, methyl acetate, benzol, chloroform, and dimethylformamide improve the stripping performances. Methanol and chloroform were the only co-solvents which improved wrinkling time at 40 per cent concentration.

System D-5 (Urea-Alkyd). In concentrations of 5 to 40 per cent methanol, 5 per cent methyl acetate, 5 to 40 per cent chloroform, and 5 per cent dimethylformamide, improved stripping action of methylene chloride was obtained.

System D-6 (Urea-Melamine). When concentrations of the following co-solvents were used, film removal was markedly less efficient: 5 to 40 per cent methanol, 5 to 40 per cent methyl acetate, 5 per cent acetone, 5 per cent "Cellosolve," and 5 per cent chloroform.

System D-7 (Silicone). Methylene chloride was extremely rapid in stripping time.

One of the best scrape-off type of paint and varnish removers can be prepared from the following formula composed by Dow Chemical Company.

Dow Methylene chloride, PRG	71	gallons
Toluene*	3	gallons
Methanol	12	gallons
Dow Di-tri-isopropanol-amine, PRG	9.5	gallons
Water	1.5	gallons
"Methocel," 4,000 CPS., PRG	13	pounds
"Areskap 100" (Monsanto Chemical Co.)	33	pounds
Potassium oleate	22	pounds
Paraffin, 122-124°F, ASTM	16.5	pounds
Triethylammonium phosphate, 40% in ethyl alcohol (Monsanto Chemical Co.)	0.5	gallons

*6.0 Gallons of VM&P naphtha can be substituted for the toluene.

Mixing:

1. Add paraffin solvent (toluene or naphtha) to the methylene chloride.
2. Melt paraffin and dissolve in the above solvents with agitation.
3. Add "Methocel" and stir until it is completely wetted out.
4. Add the methanol slowly and stir until "Methocel" is completely dispersed.
5. Add potassium oleate and "Areskap 100."
6. Add the di-tri-isopropanolamine. (If solid, warm to room temperature.)
7. Add triethylammonium phosphate.
8. Add water and mix all ingredients until uniform.

METHYL CHLORIDE

Monochloromethane

 CH_3Cl

Methyl chloride was first discovered over one hundred years ago. Its use was restricted to small-scale operation until 1920 when it came into favor as a solvent and a refrigerating agent. Since then its use has grown steadily and over forty million pounds were produced in the United States in 1953.

Methyl chloride is a moderately flammable, colorless gas at room temperature and atmospheric pressure, with a nonirritating ethereal odor. It is a stable and noncorrosive compound when in a dry state, but slowly decomposes in the presence of water to form hydrochloric acid, thus becoming corrosive to metals. It must not be placed in contact with aluminum, since it forms a spontaneously flammable methyl aluminum compound. It is readily soluble in alcohol, mineral oils, chloroform, and most organic liquids. It is insoluble in water.

It is used as a solvent and extractant for highly heat-sensitive products such as glandular products, vegetable oils, greases, and essential oils. It is

held in particular favor as a solvent and propellant for insecticides, fungicides, etc. It will dissolve nicotine, rotenone, thiocyanates, and many other insecticides. Being an excellent solvent, it is used in the manufacture of "Butyl" rubber and waterproofing compounds containing silicon, carbon compounds, etc.

PHYSICAL PROPERTIES

Acidity as HCl	0.001 % by wt, max.
Boiling point @ 760 mm	-23.8°C
Boiling range @ 760 mm	-24.6 to -23.6°C
Coefficient of cubical expansion Av./°C, liquid 0-40°C	0.0022
Critical pressure	968.7 psia 65.9 atm.
Critical temperature	289.4°F
Explosive limits in air	8.1%-17.2% by vol.
Flash point	Below 0°C
Freezing point	-97.6°C
Latent heat of evaporation @ B. P.	102.4 cal/g
Melting point	-144°F
Odor, initial	Faintly sweet, ethereal
Purity	Not less than 99%
Residue on evaporation	0.01% by wt, max.
Solubility in water @ 25°C	0.48 g/100 g
Solubility of water in solvent @ 10.76°F	0.026% by wt
Solubility in glycerin @ 77°F	0.3% by wt
Solubility of glycerin in solvent @ 77°F	0.03% by wt
Solubility in cc gas in 100 cc solvent @ 20°C, 760 mm	
Water	303
Benzene	4723
Carbon tetrachloride	3756
Glacial acetic acid	3679
Ethyl alcohol	3740

Specific gravity @20.7/4°C	1.002
Specific heat	
Liquid, 20°C	0.382 cal/g/°C
Vapor density (B. P., 760 mm)	2.47 g/liter
Weight per gallon @20.7°C	8.34 lb

TABLE 56
Vapor Pressure, Density, and Heat Content of
Liquid Methyl Chloride

TEMP. °F.	PRESSURE		DENSITY		HEAT CONTENT ABOVE -40°		
	Abs.	Gage	Liquid	Saturated vapor	Liquid	Latent	Vapor
	Lb./sq. in.		Lb./cu. ft.		B.t.u./lb.		
-40	7.40	14.86*	64.39	0.0766	0	0.4540	0.4540
-30	9.40	10.79*	63.82	0.0990	0.0080	0.4386	0.4466
-20	11.78	5.94*	63.21	0.1240	0.0160	0.4237	0.4397
-10	14.90	0.20	62.62	0.1550	0.0240	0.4093	0.4333
0	18.70	4.00	61.99	0.1930	0.0320	0.3955	0.4275
10	23.26	8.56	61.35	0.2390	0.0400	0.3822	0.4222
20	28.76	14.06	60.68	0.2920	0.0480	0.3694	0.4174
30	35.19	20.49	60.06	0.3560	0.0556	0.3570	0.4126
32	36.57	21.87	59.92	0.3716	0.0570	0.3546	0.4116
40	42.61	27.91	59.42	0.4320	0.0630	0.3449	0.4079
50	51.52	36.82	58.75	0.5203	0.0705	0.3332	0.4037
60	61.74	47.04	58.11	0.6290	0.0779	0.3216	0.3995
70	73.40	58.70	57.44	0.7410	0.0852	0.3105	0.3957
80	86.72	72.02	56.72	0.8770	0.0924	0.2996	0.3920
90	101.99	87.29	56.02	1.017	0.0994	0.2891	0.3885
100	119.04	104.34	55.34	1.181	0.1064	0.2789	0.3853
110	137.20	122.50	54.59	1.319	0.1134	0.2688	0.3822
120	155.80	141.10	53.71	1.495	0.1204	0.2586	0.3790
130	176.30	161.60	52.80	1.695	0.1274	0.2481	0.3755
140	200.00	185.30	51.81	1.905	0.1336	0.2362	0.3698

* Indicates inches of vacuum.

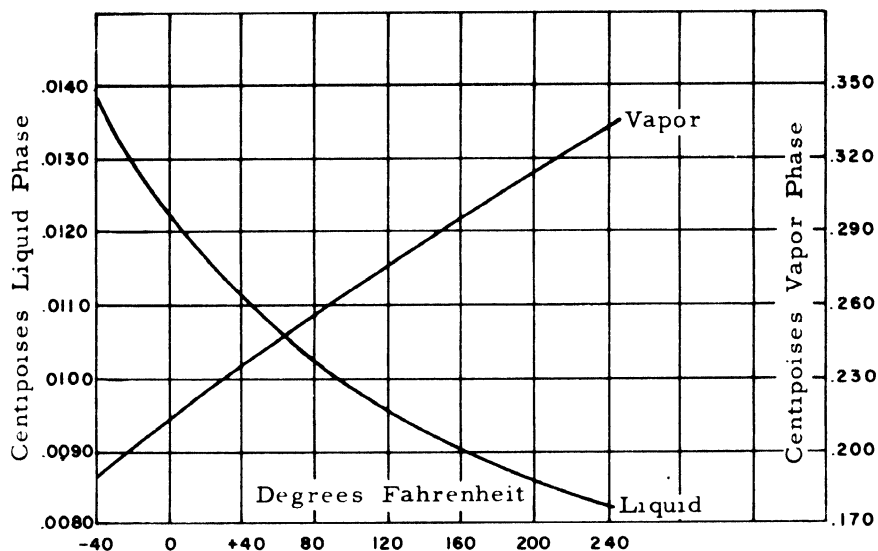
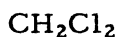


Fig. 5. Methyl chloride viscosity

DICHLOROMETHANE

Methylene chloride

Methylene dichloride



Dichloromethane is a colorless, heavy, mobile, and low-boiling liquid with a pleasant ethereal odor. It is made by the chlorination of methane and frequently contains traces of methyl chloride and chloroform. This solvent is miscible in all proportions with alcohol, ether, and chloroform and is only slightly soluble in water. It is miscible with many lacquer solvents, and is a solvent for cellulose esters and ethers. When mixed with an alcohol, ether or ester, dichloromethane has greater solvent power for alkaloids, bitumens, rubber, oils, resins, waxes, and many other organic compounds. It is used as a solvent in textile and leather coatings, where its low-boiling point and quick evaporation make it especially suitable. As a low-boiling solvent it is useful in the manufacture of artificial leather,

cellulose acetate, and in films. It is found to be useful in fire-extinguishing compositions, in the preparation of hexamethylenetetramine, as a refrigerant, as a local anesthetic, and in the extraction of oils, fats, perfumes, flavors, and drugs. It is also used as a spotting agent, degreasing medium, in the dewaxing of lubricating oils, and as an intermediate.

PHYSICAL PROPERTIES

Boiling point @ 760 mm	39.8°C 103.6°F
Coefficient of cubical expansion Av./°C, liquid (0°-40°C)	0.00137
Critical pressure	60.9 atm.
Critical temperature	237.0°C 458.6°F
Diffusivity in air (25°C, 1 atm.)	0.091 sq cm/sec
Evaporation rate (ether = 100)	71
Freezing point	-96.7°C -142.1°F
Latent heat of vaporization @ B. P.	78.7 Chu = cal/g 141.7 Btu/lb
Molecular weight	84.94
Pounds per gallon @ 20°C	11.07
Refractive index	
Liquid, n_D^{20}	1.4244
Vapor, 25°C	1.001055
Solubility in water @ 25°C	1.32 g/100 g
Solubility of water in solvent @ 25°C	0.170 g water/100 g
Specific gravity 20/4°C	1.326
Specific heat	
Liquid, 20°	0.276 cal/g/°C or Btu/lb/°F
Vapor (c_p) (B. P., 1 atm.)	0.152 cal/g/°C or Btu/lb/°F
Steam distillation point (1 atm.)	38.3°C 100.9°F
Solvent: water ratio	66.3:1 by wt
Thermal conductivity	
Liquid, 20°C	0.0888 Btu/hr (sq ft) (°F/ft)
Vapor (B. P.)	0.00437 Btu/hr (sq ft) (°F/ft)
Vapor density (B. P., 760 mm)	3.30 g/liter 0.206 lb/cu ft

Specific gravity (air = 100) 2.93

Viscosity

Liquid, 20°C
Vapor, B.P.

0.441 centipoises
0.0109 centipoises

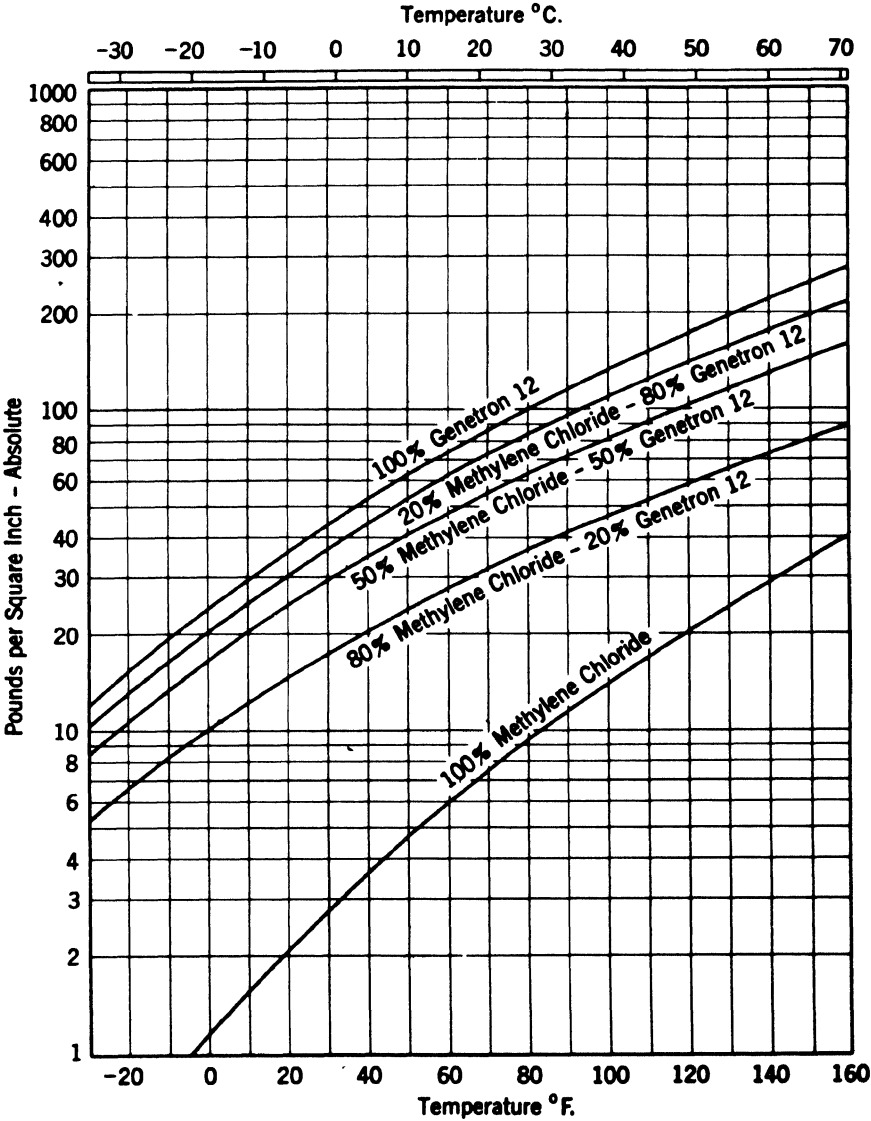


Fig. 6. Methylene chloride - "Genetron" 12 system
vapor pressure vs. temperature

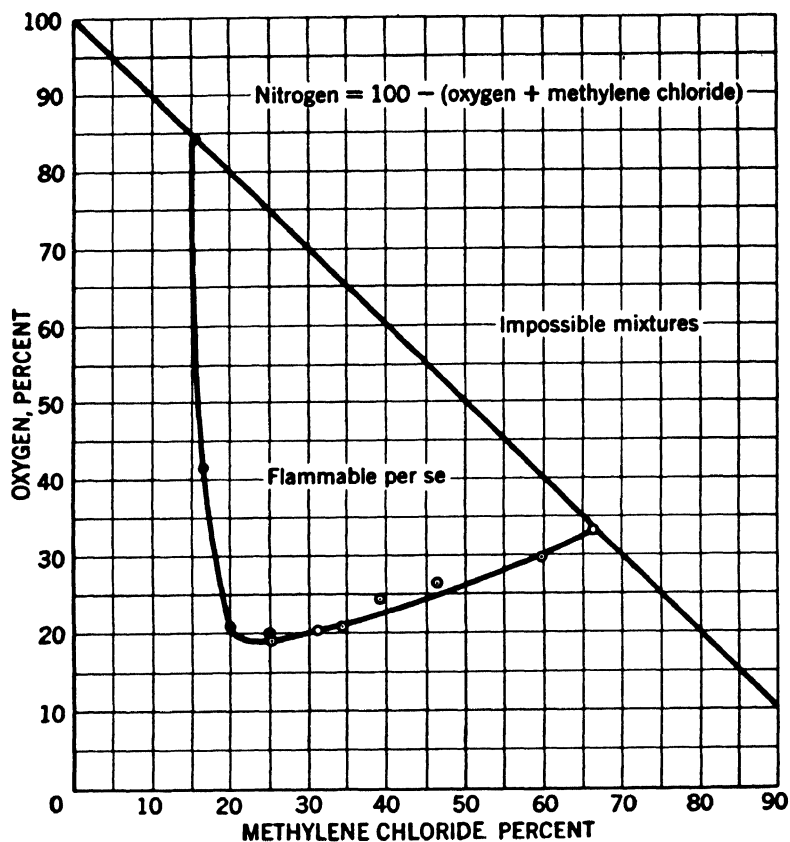


Fig. 7. Flammability of methylene chloride -oxygen-nitrogen mixtures.

1,1-DICHLOROMETHANE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
30	Acetone	57.6
23	Biallyl	56.5
94.8	1,3-Butadiene	-5.0
20	Chloromethyl methyl ether	54

30	Cyclopentane	38.0
55	Diethylamine	52.0
11.5	Ethanol	54.6
21	Iodomethane	39.8
8	Isopropanol	56.6
51	Pentane	35.5
23	Propylene oxide	40.6
6	tert-Butanol	57.1
1.5	Water	38.1

CHLOROFORM

Trichloromethane

CHCl_3

Chloroform is a heavy, water-white, volatile, and highly anesthetic liquid having a sweet odor. It is stable in the absence of water. It is soluble in ethyl alcohol, ethyl ether, and completely miscible with all halogenated hydrocarbons and most of the common solvents, but is only slightly soluble in water. It is a powerful solvent for fats, fixed, mineral and essential oils, waxes, alkaloids, resins, and tars; it is a latent solvent for cellulose derivatives. When used with a lower alcohol or ester, ethyl alcohol, or ethyl acetate, the mixture becomes a solvent for a large number of cellulose esters and ethers.

The anesthetic and toxic properties of chloroform limit its wider use as an industrial solvent. It is used medicinally in rubbing liniments and salves, as an anesthetic, as a preservative for serum, and as a vermicide. Some of its industrial uses are in plastics fabrication and film manufacture, as a cleaning and spotting agent for all textile fabrics other than those made from cellulose acetate, and as an extractant for oils, waxes, resins, rubber, sterols, etc. It is also in large demand for alkaloid assay.

PHYSICAL PROPERTIES

Acidity as HCl	0.001% by wt, max.
Boiling point	61.2°C
Boiling range @760 mm	60.0-61.5°C
Coefficient of cubical expansion Av./°C, liquid	0.001399
Color (Saybolt)	24 max.
Dielectric constant, 1000 cycle	4.90
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	63°C
Heat of evaporation @ B. P.	59.0 cal/g
Latent heat of evaporation @ B. P.	106.4 Btu/lb
Refractive index @20°C	1.4467
@25°C	1.4422
Solubility in water @20°C	0.82
Solubility of water in solvent @10°C	0.06 g/water/100 g
Specific gravity 25/25°C	1.477
Specific heat Liquid, 20°	0.234 cal/g/°C
Specific resistivity	4.0 x 10 ⁹ ohms/cm
Thermal conductivity Liquid	0.080 Btu/hr (sq ft) (°F/ft)
Vapor density (B. P., 760 mm)	4.36 g/liter
Vapor pressure @30°C	243 mm
Viscosity @20°C	5.63 millipoises
@30°C	5.10 millipoises
Water: no cloud @-10°C	0.021% by wt, max.
Weight per gallon @25°C	12.29 lb

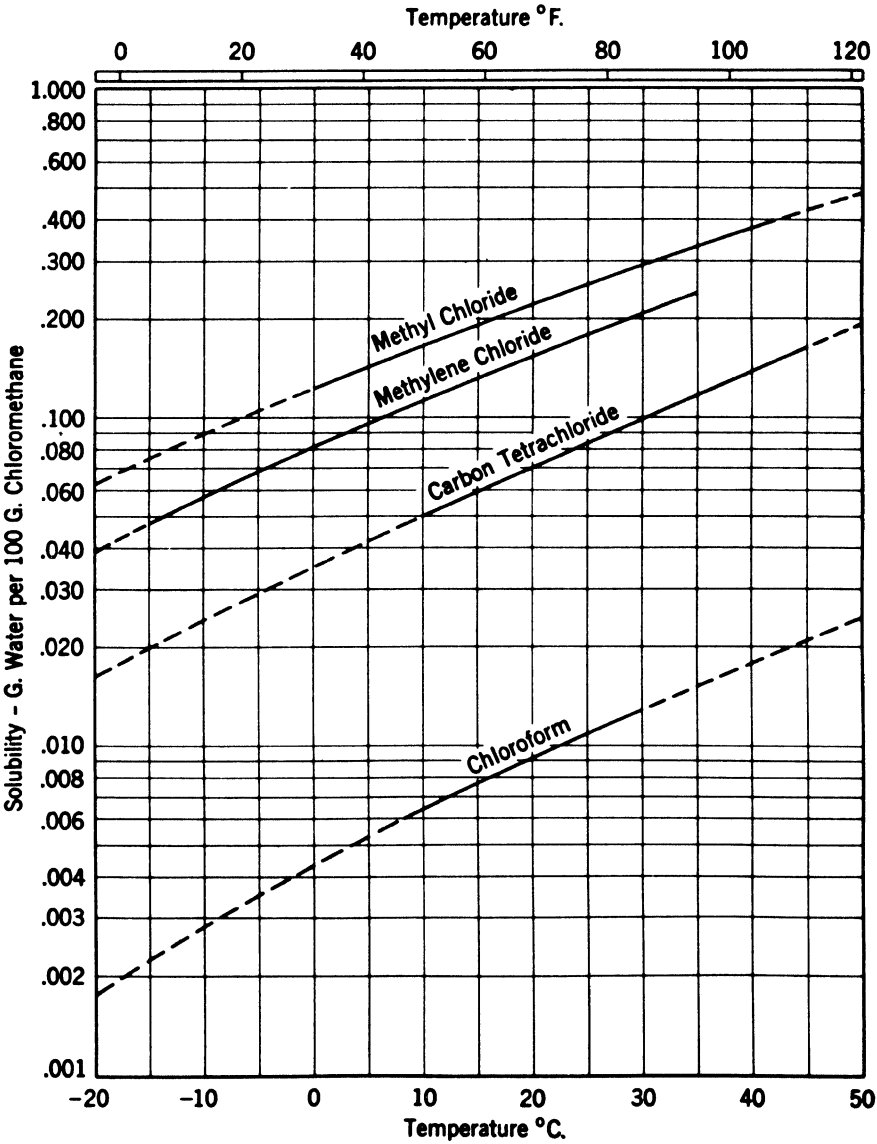


Fig. 8. Solubility of water in chloromethanes.

CHLOROFORM FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
20.5	Acetone	64.5
35	2-Bromopropane	62.2
96	2-Butanone	79.7
6.8	Ethanol	59.3
13	Ethyl formate	62.7
15	Formic acid	59.2
2.8	n-Hexane	60
4.5	Isopropanol	60.8
12.5	Methanol	53.5
23	Methyl acetate	64.8
2.8	Water	56.1

CARBON TETRACHLORIDE

Tetrachloromethane

CCl4

Carbon tetrachloride is a heavy, colorless, non-flammable, and nonexplosive liquid with a characteristic odor. It is miscible with acetic anhydride, ethyl alcohol, ethyl ether, naphtha, benzene, halogenated hydrocarbons, and with most solvents. It will dissolve fixed, mineral and essential oils, fats, greases, waxes, gums, camphor, metallic resinates, bitumens, asphalt, unvulcanized rubber, some cellulose ethers, and such resins as "Bakelite," coumarin, dammar, ester gum, elemi, guaiac, mastic, sandarac, rosin, and alkyd and vinyl resins. Its solvent power for cellulose esters and ethers is increased in the presence of a lower aliphatic alcohol or acetate. When decomposed, it may produce poisonous gases such as phosgene, chlorine, and hydrochloric acid.

Carbon tetrachloride is used extensively as a solvent and diluent, and in the extraction of oils from seeds, grease from bones and hides, and alkaloids

from plants. It is a solvent for bitumens, asphalt, gums, antimony trichloride, cholesterol, in floor waxes and furniture polish, and in paints and varnishes. It finds wide application in fire extinguishers for home and industry, in grain fumigation, moth control, as a delousing agent, as a diluent in chlorination, as a constituent part in dry cleaners' soap, and in rubber cements. It is a starting point in the synthesis of many organic chemicals, dyes, and drugs. It has the property of lowering the flammability hazard of organic solvents.

TABLE 57
Solubility of Various Dyes in Carbon Tetrachloride

DYE	MIN. CC. TO DISSOLVE 0.5 GRAM DYE	DYE	MIN. CC. TO DISSOLVE 0.5 GRAM DYE
Sudan I	5	Sudan III	20
Maroon I	5	Azo turkey red	20
Sudan VIII	5	Cloth red G	20
Chrome fast yellow	5	Sudan G	25
Rose	5	Maroon II	25
Sudan VII	5	Cloth red BB	25
Scarlet H	5	Fast brown O	25
Walnut	5	Maroon III	25
Sudan II	5	Sudan brown	25
Xylidine brown	5	Chrysamine G	25
Indiana red	5	<i>p</i> -Nitroaniline red	35
Oil maroon	5	Alizarin yellow R	35
Azo coccine RR	8	Aniline yellow G	35
Xylidine red N	8	Cardinal	35
Xylidine brown M	10	Benzidine puce	35
Sudan IX	10	Benzidine puce A	35
Sudan X	10	Indoine blue	35
Naphthol black	10	Congo red A	60
Oil Scarlet	10	<i>m</i> -Nitroaniline orange	60
Sudan R	15	Alizarin yellow GG	60
Fast Red A	15	Benzidine brown	100 Inc.
Oil brown	15	Diazine green	100 Inc.
Spirit yellow	20	Diazine black	100 Inc.

PHYSICAL PROPERTIES

Acidity as HCl	None
Boiling point @ 760 mm	76.7°C (170.1°F)
Boiling range	Within 1°C
Coefficient of cubical expansion Av./°C, liquid	0.00127

Dielectric constant, 1000 cycle	2.24
Electrical conductivity	4×10^{-18} recip. ohm
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	-23°C
Heat of fusion	4.2 cal/kg
Heat of vaporization	46.5 cal/g
Power factor, 1000 cycle	0.057%
Purity	99.99% min.
Refractive index @20°C	1.4607
Residue	0.0010% by wt, max.
Solubility in water @20°C	0.08% by wt
Solubility of water in solvent @20°C	0.008% by wt
Specific gravity @25/4°C	1.5845
Specific heat	
Liquid, 25°	0.1995 cal/g/°C
76.8°C	0.2157 cal/g/°C
Specific resistivity	3.8×10^{12} ohms/cm
Thermal expansion per °C	0.127% (of liquid @158°F)
Vapor density (B.P., 760 mm)	5.37 g/liter
Vapor pressure @30°C	140 mm
Viscosity liquid @20°C	0.96 centipoise
Weight per gallon @25°C	13.22 lb

CARBON TETRACHLORIDE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
88.5	Acetone	56.4
	Acetonitrile	71
3	Acetic acid	76.55
21	Acrylonitrile	66.2
11.5	Allyl alcohol	72.3
71	2-Butanone	73.8
4.5	tert-Amyl alcohol	76.6
2.5	Butyl alcohol	76.6
7.6	sec-Butyl alcohol	74.6

24	tert-Butyl alcohol	70.5
35	Butyl nitrite	74.8
21	1, 2-Dichloroethane	75.6
43	Ethyl acetate	74.8
15.85	Ethyl alcohol	61.1
15.5	Ethyl nitrate	75
81.5	Formic acid	66.65
5.5	Isobutyl alcohol	75.8
12	Isopropyl alcohol	69
20.56	Methanol	55.7
25	Methyl propionate	76
17	Nitromethane	71.3
11.5	Propyl alcohol	73.1
31	Propyl formate	74.6
4.1	Water	66

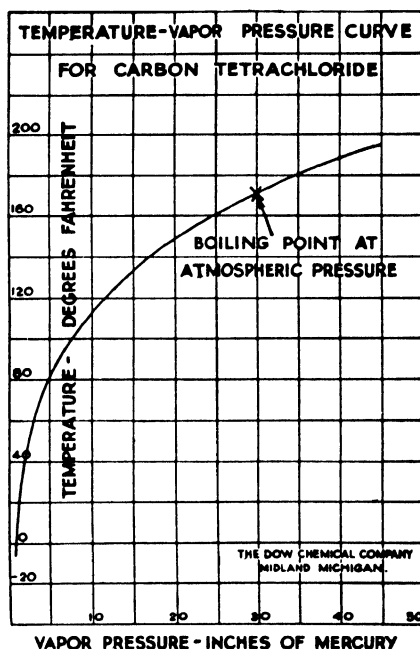


Fig. 9. Temperature-vapor pressure curve for carbon tetrachloride.

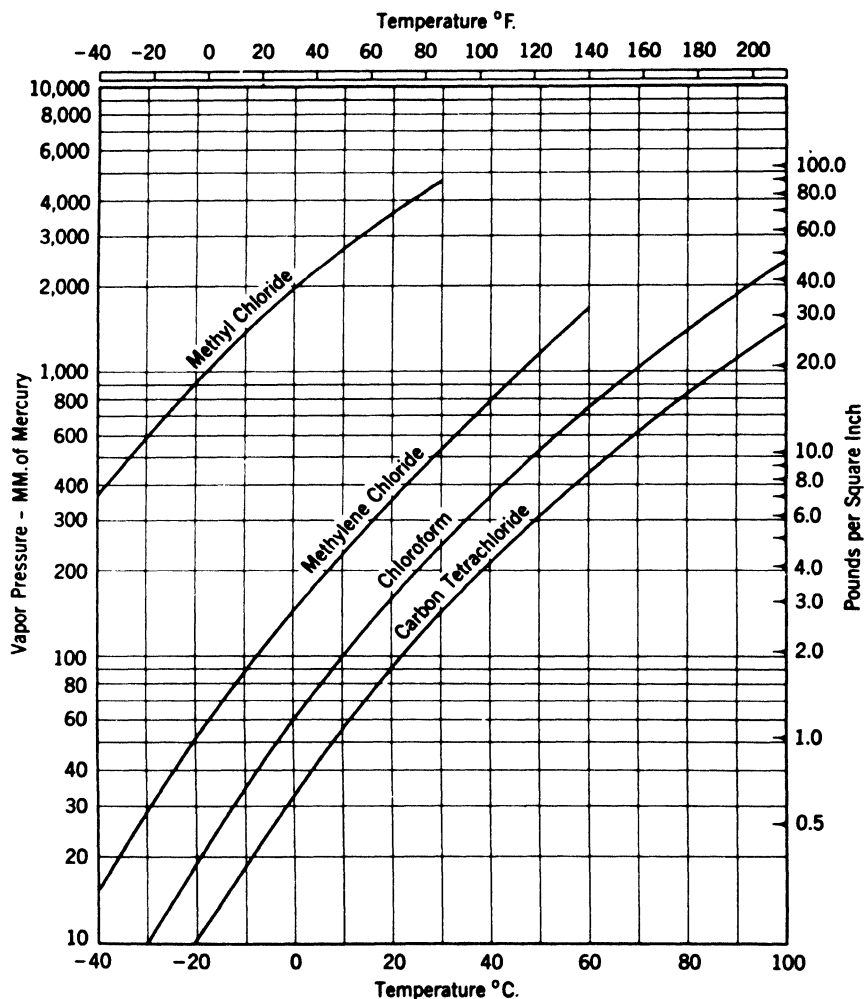
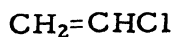


Fig. 10. Chloromethanes

VINYL CHLORIDE

Monochloroethylene



Vinyl chloride is a water-white liquid which, when under pressure, is easily volatilized to a flammable gas having an odor much like that of ethyl chloride. It is only slightly soluble in water but sol-

uble in ethyl alcohol, ethyl ether, and carbon tetrachloride. It is used widely in the production of certain plastics, as a refrigerant, as a special solvent, and for organic synthesis.

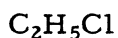
PHYSICAL PROPERTIES

Acetaldehyde	Not more than 0.5% by wt
Boiling point @760 mm	-13.9°C
Boiling range @760 mm	Not less than 95% distills over before the temperature of the liquid reaches 10°C
Color	Water-white
Freezing point	-159.7°C
Heat of evaporation	81.6 cal/g
Residue	Not more than 0.5% by vol.
Specific gravity @B. P.	0.97
Specific heat	0.27 cal/g/°C
Solubility in water @25°C	Slightly soluble
Weight per gallon @20°C	7.59 lb

ETHYL CHLORIDE

Monochloroethane

Muriatic ether



Ethyl chloride is a colorless, volatile, and flammable liquid having an ether-like odor. In the absence of water it is stable and noncorrosive, but it hydrolyzes in the presence of water or alkalies. It is miscible with ethyl ether, carbon tetrachloride, and most of the commonly used solvents; it is partially soluble in ethyl alcohol and only slightly soluble in water. It is a solvent for phosphorus, fats, oils, resins, waxes, etc. It is used as a solvent, a local anesthetic, insecticide, refrigerant, in the preparation of dyes and drugs, and as an ethylating agent. Adding a lower aliphatic alcohol or acetate greatly improves the solvent power of ethyl chloride and other chlorinated ethanes such as the dichloro-, trichloro-,

tetrachloro-, and pentachloroethanes. Combined with methyl alcohol and benzene it will dissolve nitrocellulose, and combined with methyl acetate it will dissolve triethylcellulose.

PHYSICAL PROPERTIES

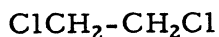
Acidity as HCl	0.0002% by wt, max.
Boiling point	12.3°C
Boiling range @ 760 mm	12.2-12.6°C
Coefficient of expansion Av./°C, liquid	0.0021
Critical point	187°C and 52 atm.
Dielectric constant Liquid @ 170°C	6.29
Flash point	Below 32°F
Freezing point	-139°C
Heat of combustion (gas)	316.7 kg cal/mol.
Latent heat of evaporation @ B. P.	92.5 cal/g or 165.6 Btu/lb
Nonvolatile matter	0.001% by wt, max.
Purity	Contains less than 0.04% acid and less than 0.05% alcohol
Refractive index @ 0°C	1.1179
Solubility in water @ 20°C	0.574 g/100 g solvent
Solubility of water in solvent @ 21°C	48.3 g/100 g solvent
Specific gravity @ 0/4°C	0.923
Specific heat @ 0°C	0.37 cal/g or Btu/lb
Vapor density (B. P., 760 mm)	2.76 g/liter
Vapor pressure @ -30°C	107.4 mm
@ -20°C	180.3 mm
@ -10°C	289.1 mm
@ 0°C	450 mm
@ 10°C	678 mm
@ 20°C	1000 mm
Viscosity liquid @ 20°C	0.1 centipoise
Water content, no cloud @ -15°C	0.011% by wt, max.
Weight per gallon @ 0°C	7.70 lb

ETHYLENE DICHLORIDE

1,2-Dichloroethane

sym-Dichloroethane

Ethylene chloride



Dutch oil

Elayl chloride

The synonym "Dutch Oil" owes its origin to the four Dutch chemists who, in 1795, were first to prepare this compound. It is a colorless, stable, volatile, and mobile liquid resembling chloroform in its odor and toxicity; it is manufactured by the chlorination of ethane or ethylene. It is insoluble in water, but soluble in ethyl alcohol, ethyl ether, carbon tetrachloride, and it is miscible in all proportions with most common solvents. Ethylene dichloride is a good solvent for oils, fats, waxes, some alkaloids, unvulcanized rubber, camphor, benzyl abietate, coumarone resins, dammar, guaiac resin, mastic, rosin, sandarac, phenolic, acrylic and vinyl resins, metallic resinates, gums, etc., and it will dissolve some cellulose ethers. Its solvent power is greatly improved for a large number of cellulose ethers and esters when it is mixed with ethyl or methyl alcohol, or ethyl or methyl acetate. Since ethylene dichloride shows satisfactory stability toward hydrolysis under normal conditions of usage, its desirability as a solvent is receiving wider attention. It is resistant to oxidation, does not corrode metals, and burns with difficulty, though it supports combustion.

This cheap and readily available solvent is extensively used in the extraction of edible oils from oil-bearing seeds, vitamins from fish-liver oils, and residual oil from oil cakes. A mixture composed of three parts ethylene dichloride and one part carbon tetrachloride is used as a nonexplosive, noninjurious fumigant for furniture, furs, cereals, grains, flour,

dried fruit, and nuts. It is a component of lead tetra-ethyl anti-knock fluid and is used in the extraction of pyrethrum flowers. It is also employed in the textile industry for degreasing wool, as a spotting agent for the removal of tar, paint, and brand marks, in soap scouring compounds, and in wetting out, penetrating, and degumming compounds. In combination with carbon tetrachloride, it is used in dry-cleaning and spotting fluids. It is used as a lacquer solvent, in paint, varnish and finish removers, in degreasing metals, and in chemical synthesis. It is also an extractive agent for nicotine from tobacco.

PHYSICAL PROPERTIES

Acidity as HCl	Not more than 0.001%
Apparent ignition temperature in air	449°C
Boiling point	83.6°C
Boiling range @ 760 mm	Below 82.5°C none Above 84.0°C none
Coefficient of cubical expansion Av./°C, liquid (10-30°C)	0.00116
Color (500-mm tube) (Lovibond)	Not more than 1.0 yellow
Dielectric constant @ 20°C	10.5±0.3
Electrical conductivity	3×10^{-8}
Explosive limits in air	6.2-15.9% by vol.
Fire point	28°C
Flash point (ASTM O. C.)	21°C
Freezing point	-35°C
Heat of combustion	2720 cal/g
Latent heat of evaporation @ B. P.	77.3 cal/g
Nonvolatile matter	Not more than 0.001 g/100 cc
Purity	Not less than 99.0%
Refractive index	1.4443

Solubility in water @20°C	0.87 % by wt
Solubility of water in solvent @20°C	0.16% by wt
Specific gravity @20/20°C	1.2550
Specific heat	0.31 cal/g/°C
Specific resistivity	9.0 x 10 ⁶ ohms/cm
Surface tension @25°C	37.5 dynes/cm
Thermal conductivity @20°C	0.0038 cal/cm/sec/°C
Vapor density (B.P., 760 mm)	3.88 g/liter
Vapor pressure @20°C	63 mm
@30°C	99 mm
Viscosity @25°C	0.0078 poise
Water content	Not more than 0.02%
Weight per gallon @25°C	10.38 lb

ETHYLENE DICHLORIDE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
18	Allyl alcohol	79.9
6	tert-Amyl alcohol	83
79	Carbon tetrachloride	75.6
19.5	1,1-Dichloroethane	72
37	Ethanol	70.3
38	Formic acid	77.4
6.5	Isobutanol	83.5
43.5	Isopropyl alcohol	74.7
19	Propanol	80.7
10	n-Propyl formate	84.1
18	Trichloroethylene	82.9
32	Methanol	61
8.2	Water	70.5

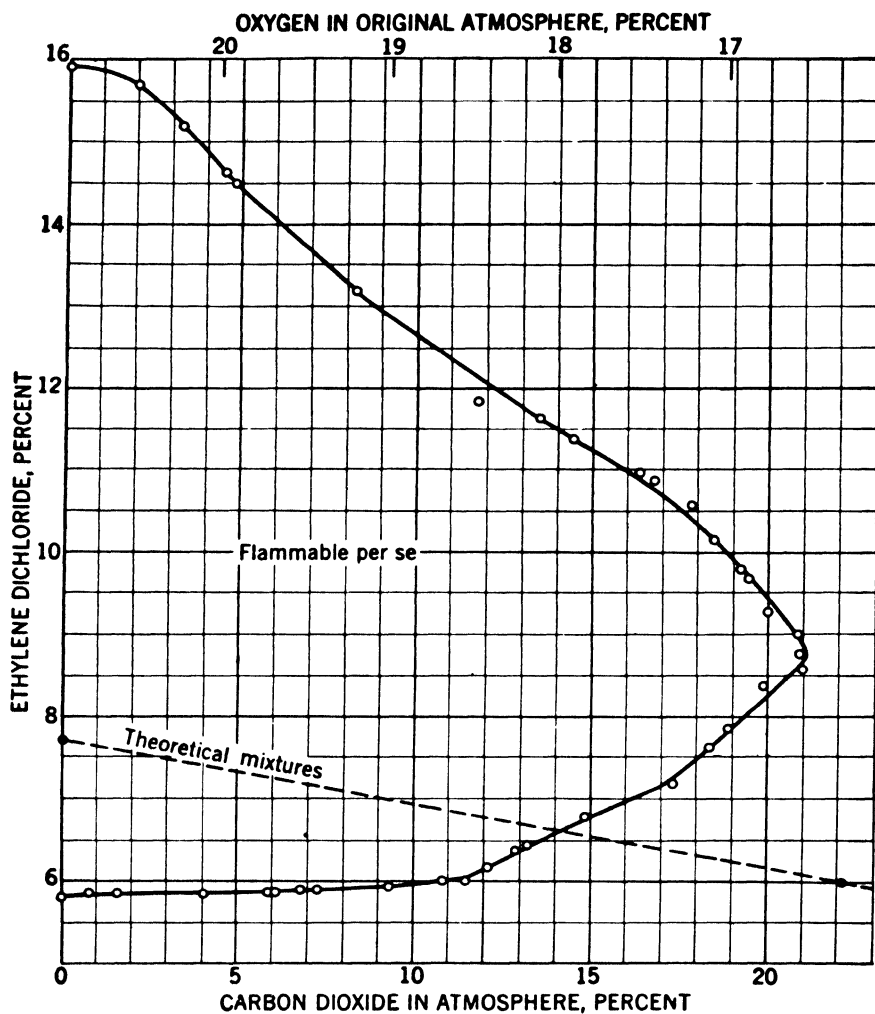


Fig. 11. Limits of flammability of ethylene dichloride in air and carbon dioxide.

SOLUBILITY

Chlorinated Compound	Hydrocarbons	Lin-seed Oil (raw)	Cellulose Acetate	Nitrocellulose	"Vynlite" Resins AYAF VYHH	Shel-lac	Kauri Gum	Dewaxed Dammar	Rosin	Ester Gum	Unvulcanized Rubber
Ethylene dichloride	S	S	SA	SA	S	I	I	S	S	S	S
Propylene dichloride	S	S	I	SA	S	I		S	S	S	S
Trichloroethane	S	S	I	I	S	PSW	PS	S	S	S	PSG
Trichloroethylene	S	S	I	I	S	PS	PS	S	S	S	S
n-Butyl chloride	S	S	I	I	S	PSW	PS	S	S	PS	PS
Dichloroethyl ether	S	S	SA	SA	S	I	I	I	S	S	I
Dichloroisopropyl ether	S	S	I	I	S	PSW	SW	S	S	S	PSG
Triglycol dichloride	S	S	PSA	SA	S	SW	PSW	SW	S	S	I
2-Ethylhexyl chloride			I	I	I	I			S	S	E
Dichloroethyl formal			I	E	S	I			S	S	I

S - Soluble

PS - Partly Soluble

SA - Soluble with alcohol

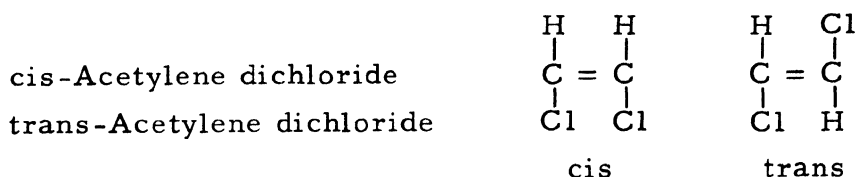
I - Insoluble

W - Warm

G - Soluble, but prone to gel formation

E - Swells

DICHLOROETHYLENE



Dichloroethylene is a mixture of stereoisomeric compounds obtained by the partial chlorination of acetylene. Its physical properties are determined by the different isomers present in its composition. It is a colorless, low-boiling liquid with a pleasant odor. The hot vapors of this solvent can be ignited, but it will not continue to burn unless heat is supplied. Nevertheless, there is little danger present in its general use. It is soluble in ethyl alcohol, ethyl ether, benzene, and carbon tetrachloride, but insoluble in water. It is a good solvent for oils, gums, resins, waxes, unvulcanized rubber, shellac, and cellulose acetate. When mixed with ethyl or methyl alcohol or alkyl acetates, it shows a pronounced solvency for the ester and ether derivatives of cellulose. It is used in the extraction of dyes, perfumes, and organic material, in lacquers, thermoplastics, and as a rubber solvent.

PHYSICAL PROPERTIES

cis isomer

Acidity as HCl	0.0005% by wt, max.
Boiling point @ 760 mm	60.3°C
Coefficient of cubical expansion Av./°C, liquid	0.00127
Color (Saybolt)	24 max.
Flash point	6°C
Freezing point	-80.5°C
Latent heat of vaporization @ B. P.	73.0 cal/g
Refractive index @ 15°C	1.4519
Residue on evaporation	0.007% by wt, max.

Solubility in water @25°C	0.77 g/100 g
Solubility of water in solvent @10°C	0.04 g water/100 g
Specific gravity @20/4°C	1.282
Specific heat Liquid, 20°C	0.270 cal/g/°C
Vapor density (B. P., 760 mm)	3.54 g/liter
Vapor pressure @30°C	273 mm
Viscosity liquid @20°C	0.48 centipoise
Water: no cloud @-15°C	0.001% by wt, max.
Weight per gallon @20°C	10.70 lb

PHYSICAL PROPERTIES

trans isomer

Acidity as HCl	0.0005% by wt, max.
Boiling point @760 mm	48.0-48.5°C
Boiling range @760 mm	47.0-48.5°C
Coefficient of cubical expansion Av./°C, liquid	0.00136
Color (Saybolt)	24 max.
Flash point	4°C
Freezing point	-50°C
Latent heat of vaporization @B. P.	73.7 cal/g
Refractive index @15°C	1.4490
Residue on evaporation	0.0007% by wt, max.
Solubility in water @25°C	0.63 g/100 g
Solubility of water in solvent @10°C	0.03 g water/100 g
Specific gravity @20/4°C	1.257
Specific heat Liquid, 20°C	0.270 cal/g/°C
Vapor density (B. P., 760 mm)	3.67 g/liter
Vapor pressure @30°C	395 mm
Viscosity liquid @20°C	0.41 centipoise
Water: no cloud @-15°C	0.004% by wt, max.
Weight per gallon @20°C	10.49 lb

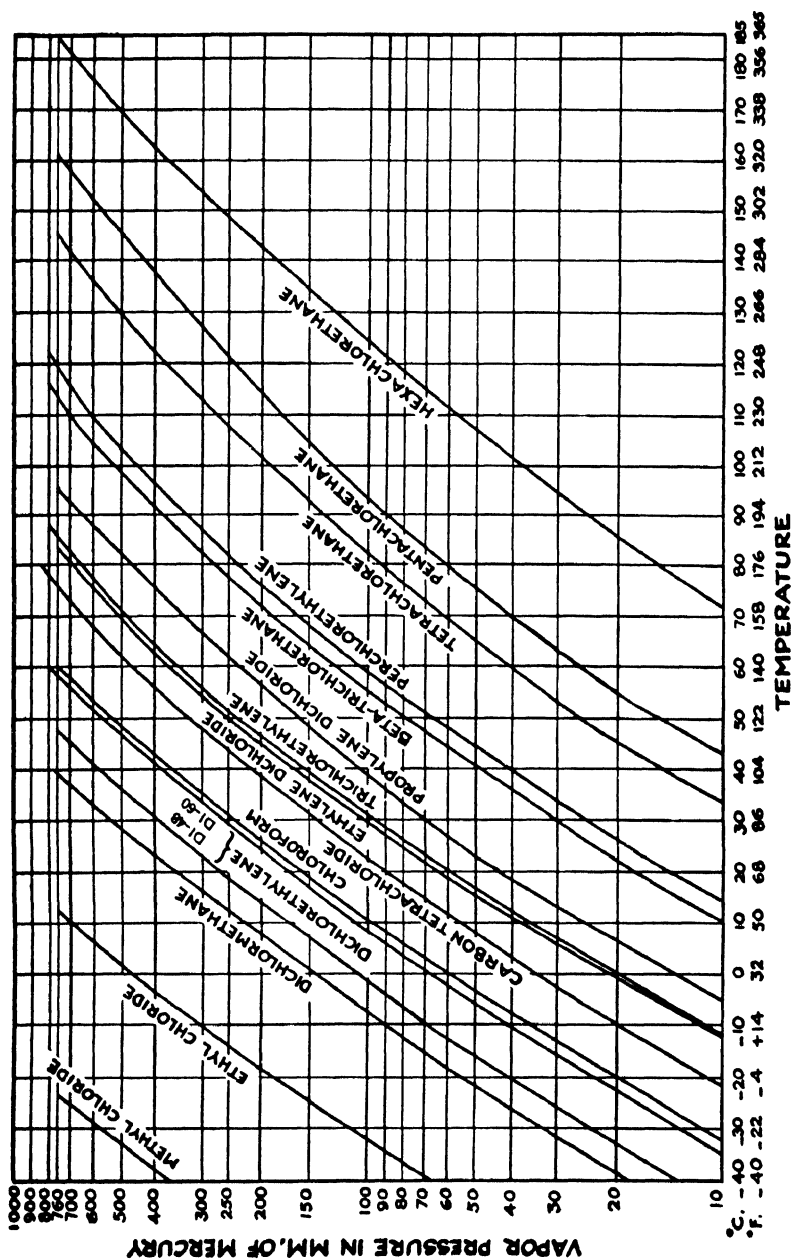


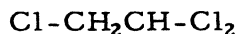
Fig. 12. Vapor pressure of various solvents at different temperatures

TRICHLOROETHANE

1, 1, 2-Trichloroethane

beta-Trichloroethane

Vinyl trichloride



Ethylene trichloride

Trichloroethane is a colorless and volatile liquid, soluble in alcohol, ether, and most organic solvents, but it dissolves in water with difficulty. It is stable under ordinary conditions and is a good solvent for cellulose acetate and most oils, fats, and waxes, as well as natural rubber and certain types of synthetic rubber. It therefore offers possibilities as an extractant and for other applications carried out in closed or well-ventilated systems where toxic quantities are prevented from being vaporized. By splitting off hydrogen chloride, trichloroethane is converted to vinylidene chloride ($\text{CH}_2=\text{CCl}_2$), used in the manufacture of resins. The Underwriters' Laboratories standard of classification lists this solvent as nonflammable at ordinary temperatures. Its fire hazard is very small as shown by the following comparative ratings: trichloroethylene, 1; trichloroethane, 3; ethylene dichloride, 60 to 70; gasoline, 90 to 100; ether, 100. Trichloroethane has a local irritating effect on the eyes and the mucous membrane of the nose; it is narcotic even in low concentrations. It is less toxic than alpha-trichloroethane, and tetrachloroethane (acetylene tetrachloride), but more toxic than trichloroethylene, ethylene dichloride, or carbon tetrachloride.

PHYSICAL PROPERTIES

Acidity as HCl	0.0001% by wt, max.
Boiling point @ 760 mm	113.5°C
Boiling range @ 760 mm	111.8-113.3°C (5-95%)
Fire point	Nonflammable
Flash point	Nonflammable
Free halogen	None

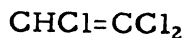
142 SOURCE BOOK OF INDUSTRIAL SOLVENTS

Freezing point	-36.7°C
Latent heat of evaporation @B. P.	68.7 cal/g
Nonvolatile matter	None
Refractive index	1.4711
Solubility in water @25°C	0.48 g/100 g
Solubility of water in solvent @20°C	0.03 g water/100 g
Specific gravity @20/4°C	1.441
Specific heat Liquid, 20°C	0.266 cal/g/°C
Specific resistivity	5.2×10^8 ohms/cm
Vapor density (B. P., 760 mm)	4.21 g/liter
Vapor pressure @30°C	36 mm
@90°C (194°F)	369 mm
@100°C (212°F)	505 mm
@110°C (230°F)	680 mm
@114°C (237°F)	764 mm
Water	0.007% by wt, max.
Weight per gallon @20°C	12.04 lb

TRICHLOROETHYLENE

1,2,2-Trichloroethylene

"Westrosol"



Tri

Trichloroethylene is a heavy, low-boiling, colorless, and mobile liquid with a pleasant and chloroform-like odor. It is quite stable, nonflammable, nonexplosive, and it will not attack the common metals even in the presence of moisture. The first record of its preparation was in 1864 by the reduction of hexachloroethane with hydrogen. Germany started commercial production in 1910, and the United States is now producing it on an extensive scale.

It is insoluble in water, but is soluble in most organic solvents, some of which are acetone, ethyl ether, benzene, toluene, pyridine, amyl, butyl, ethyl and methyl acetates or alcohols and mixtures of these

solvents. It dissolves cellulose ethers and some types of cellulose acetate. Mixed with cyclohexanol or p-toluene sulfonamide, this solvent is particularly effective with cellulose esters and ethers. It is a solvent for chewing gum, crude rubber, dyes, bitumens, pitch, sulfur, chlorinated hydrocarbons, stearic acid, oils, fats, waxes, grease, tar, gums, caffeine, and such resins as ester gum, rosin, coumarone, mastic, elemi, and vinyl.

It is considered by many as the "ideal solvent" because it so nearly fulfills all the requirements of the perfect solvent as summarized by such properties as:

High solvent power	Nonflammability
Rapid rate of penetration	Low specific gravity
Ease of separation from extracted matter	Low latent heat of vaporization
Economical recovery	Low specific heat
High stability	Optimum boiling point
Low toxicity	

It is used in the extraction and purification of olive, maize, linseed, soybean and other edible and inedible oils from the press cake or native material, as well as of mineral and vegetable waxes, cocoa butter, fats, nicotine, greases from tankage, bones and leather, and caffeine from coffee. It is used as a fat solvent in analytical procedures and as a means of separating formic acid from acetic acid. It is used as an insecticide in combination with soap to destroy the larvae and pupae of such stinging and aquatic insects as mosquitoes and grape lice, and it is effective as a disinfectant and cleaner of vermin-infested clothes and floors. It is also applied as a fumigant.

It is employed in both the liquid and vapor phase for degreasing metal surfaces, glass, dishes, films, molded articles, leather, textiles, raw wool, machinery, and for dewaxing mineral oils. It is used as a cleaning agent in electroplating metal parts, in the

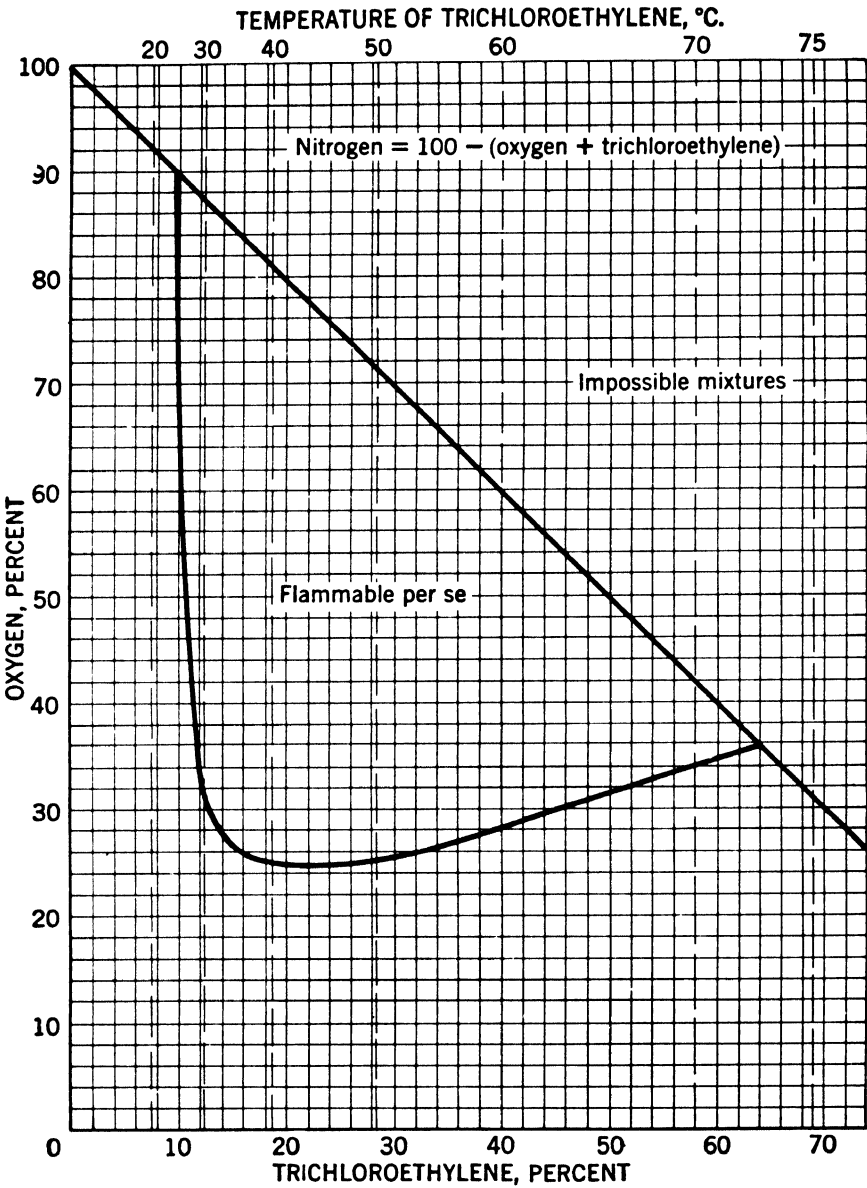


Fig. 13. Flammability of trichloroethylene, oxygen, and nitrogen mixtures.

printing, paint, automobile, textile, and leather industries, and in the dry-cleaning industry where it cleans rapidly, making prespotting unnecessary, and assuring freedom from fire hazard.

It is also used in making wet soap, neutral and liquid soaps, egg-covering compounds, degreasing and depitching compounds, paint, varnish, tar removers, household cleaning compounds, rubber cements, shoe and stove polishes. As an intermediate, it is used in the manufacture of dyes, pharmaceuticals, perfumes, and organic chemicals. It is a general solvent for oils, fats, greases, waxes, tar, rubber, gums, and resins, and it is used as a laboratory agent; it has wide application as a volatile thinner for paints, lacquers, and thermoplastics. It is also a refrigerant, and an anthelmintic.

There are reports that trichloroethylene is soluble with many cellulose acetate silk dyes that cause bleeding. The colors which are most affected are the yellows, oranges, reds, and violets. The blues are less affected and the blacks are practically unaffected. The majority of vat dyes are only slightly affected. Indigoid vat dyes bleed more readily than the anthraquinone type. Azoic colors bleed quite badly. However, the following colors show little or no bleeding: basic cotton dyes, basic, acid, direct and mordant silk dyes, and sulfur viscose dyes.

PHYSICAL PROPERTIES

Acidity as HCl	Not more than 0.001%
Boiling point	86.7°C
Boiling range @ 760 mm	95% or better distills from 86.0-87.5°C
Coefficient of expansion per °C	0.00115-20°C
Color (Saybolt)	24 max.
Dielectric constant, 1000 cycle	3.27
Fire point	Nonflammable
Flash point (ASTM O. C.)	None @ B. P.
Free chlorine	None

Freezing point	-86.4°C
Latent heat of vaporization @ B. P.	57.3 cal/g
Nonvolatile matter	0.00067% by wt, max.
Power factor, 1000 cycle	2.2%
Refractive index @27°C	1.4735
Solubility in water @25°C	0.10% by wt
Solubility of water in solvent @25°C	0.02% by wt
Specific gravity @20/20°C	1.4655
Surface tension @25°C	32.0 dynes/cm
Vapor pressure @ -20°C	4.5 mm
@ - 9°C	9.0 mm
@ 0°C	17.4 mm
@ 20°C	56.0 mm
@ 40°C	145 mm
@ 50°C	230 mm
@ 65°C	385 mm
@ 77°C	562 mm
Viscosity @25°C	0.00550 poise
Water content	0.002% by wt
Weight per gallon @20°C	12.20 lb

TRICHLOROETHYLENE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
3.8	Acetic acid	87.0
16	Allyl alcohol	81.0
7.5	tert-Amyl alcohol	86.7
2.5	Butanol	86.9
33	tert-Butanol	75.8
12	1,2-Dichloroethane	82.9
46.5	Diethoxymethane	89.29
8	Isobutanol	85.4
30	Isopropanol	75.5
17	Propanol	81.8
80	Propyl formate	79.5
27	Ethanol	70.9

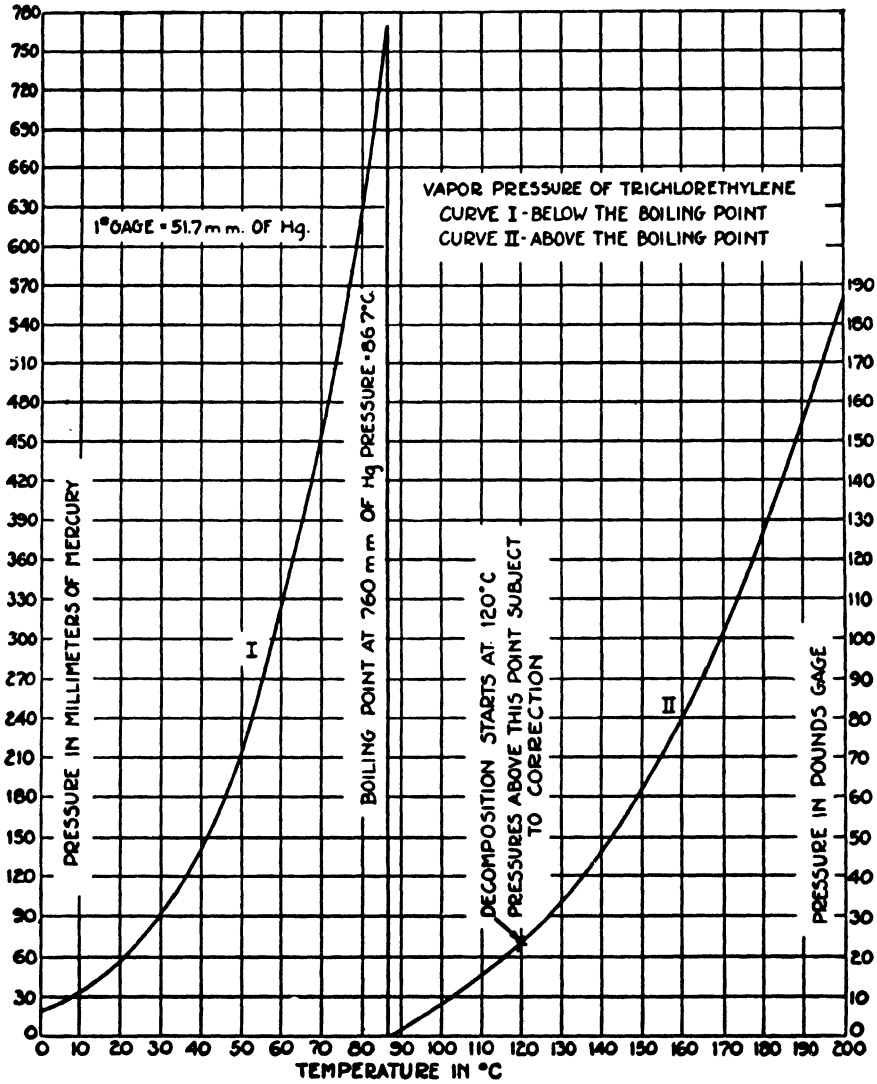


Fig. 14. Vapor pressure of trichloroethylene, at various temperatures.

1, 1, 1-TRICHLOROETHANE

Chloroethene

Methyl chloroform



This is an inhibited, nonflammable solvent, soluble in acetone, benzene, carbon tetrachloride, methanol, and ether but insoluble in water. It is a good solvent for grease and oil and excellent for cold degreasing of metal. However, it has very little effect on electrical insulating varnishes. It is considered the least toxic of the chlorinated aliphatic hydrocarbons. It has a tendency to hydrolyze slowly in the presence of water at elevated temperatures although hydrolysis at room temperature is slight.

PHYSICAL PROPERTIES

Acidity as HCl	Not over 0.001% by wt
Average weight per gallon @ 77°F	10.97 lb
Boiling range @ 760 mm Hg	
IBP	162°F
5%	163°F
95%	183°F
D. P.	190°F
Color	Not more than 15 Pt-Co. scale
Distillation (760 mm)	72-88°C
Fire point	None
Flash point	None
Freezing point	-35°F
Maximum allowable concentration in air	500 ppm
Molecular weight (pure)	133.4
Nonvolatile matter	Not over 0.001% by wt
Refractive index @ 77°F	1.4347
Specific gravity @ 25/25°C	1.312-1.321
Water	0.01% by wt, max.
Vapor pressure @ 68°F	101 mm Hg

1, 1, 2, 2, -TETRACHLOROETHANE

Acetylene tetrachloride

Bonoform

 $\text{CHCl}_2\text{-CHCl}_2$

"Cellon"

1, 1, 2, 2, -Tetrachloroethane is a heavy, colorless, and mobile liquid that is nonflammable, corrosive, and toxic, possessing a mildly chloroform-like odor. It is made by the chlorination of ethane, acetylene, or ethylene, and it has the highest solvent power of the chlorinated hydrocarbons. It is soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride, and many organic solvents and liquids, but is insoluble in water. It dissolves oils, fats, waxes, gums, resins, bitumen, pitch, tarry material, sulfur, phosphorus, halogens, cellulose acetate and nitrate, crude rubber, dyes, camphor, shellac, and many other organic substances. By adding it to a lower aliphatic alcohol or acetate, its solvency for nitrocellulose and cellulose acetate is improved. It is more toxic than chloroform and contact with its vapors will induce abnormal fatigue and nausea; prolonged exposure will cause jaundice and enlargement of the liver. Its commercial applications are limited because of its toxicity. It is used, however, in the preparation of lacquers and varnishes; in mixtures for the removal of paint, varnish, and finishes; and in the manufacture of photographic films, smoke-producing compounds, and imitation pearls.

PHYSICAL PROPERTIES

Acidity as HCl	0.0027% by wt, max.
Boiling point	146.5°C
Coefficient of cubical expansion Av./°C, liquid	0.000998 (15-99°C)
Fire point	Nonflammable
Flash point	Nonflammable
Free halogen	None

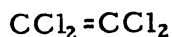
Freezing point	-43°C
Heat of vaporization @B. P.	55.1 cal/g
Refractive index	1.4942
Residue on evaporation	0.00062% by wt
Solubility in water @25°C	0.32% by wt
Solubility of water in solvent @20°C	0.03% by wt
Vapor pressure @30°C	9 mm
Viscosity liquid @20°C	1.7 centipoises
Water: no cloud @-10°C	0.032% by wt
Weight per gallon @25°C	13.25 lb

1, 1, 2, 2-TETRACHLOROETHANE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
45	Butyl propionate	152.5
3.8	Butyric acid	145.7
1.8	Chloroacetic acid	146.3
55	Cyclohexanone	159.1
74	2-Ethoxyethyl acetate	158.2
27	Ethyl chloroacetate	147.5
39	Ethyl orthoformate	151.5
97	2-Furaldehyde	161.6
9	Glycol	145.1
32	Isoamyl acetate	150.1
98	Isoamyl alcohol	131.3
37	Isobutyl isobutyrate	144.9
7	Isobutyric acid	144.8
15	Mesityl oxide	147.5
52	Methyl lactate	143.3
60	Propionic acid	140.4
34	Propyl butyrate	150.2
45	Styrene	143.5

TETRACHLOROETHYLENE

Perchloroethylene



Tetrachloroethene

Tetrachloroethylene was first prepared by Faraday in 1821. It is a heavy, colorless liquid, stable, nonflammable, toxic, narcotic, and slightly corrosive to metals with an ether-like odor. It is soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride, and most organic solvents, but is insoluble in water. The miscibility and solvency of tetrachloroethylene are similar to those of trichloroethylene, serving as a substitute for the latter where a slower rate of evaporation is desired. When either of these compounds is mixed with an active solvent, the mixture will dissolve cellulose esters and ethers. It is an outstanding dry-cleaning fluid. It is used in fire extinguishing compounds, as a liquid medium in high-tension switches and transformers, and as a general solvent. In 1953, production had reached about 153,000,000 pounds.

PHYSICAL PROPERTIES

Acidity as HCl	0.001% by wt, max.
Boiling point	121.0°C
Boiling range @ 760 mm	120-122°C
Coefficient of cubical expansion Av./°C, liquid	0.001079 (15-90°C)
Color (Saybolt)	22
Dielectric constant, 1000 cycle	2.20
Dielectric strength, 0.1° gap	30,000 volts
Explosive limits	None
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	-22.4°C
Latent heat of vaporization @ B. P.	50.1 cal/g
Nonvolatile matter	0.0007% by wt, max.
Power factor, 1000 cycle	0.02%

Refractive index	1.5055
Residue on evaporation	0.0106% by wt, max.
Solubility in water @25°C	0.04% by wt
Solubility of water in solvent @20°C	0.02% by wt
Specific gravity @25/25°C	1.618
Specific heat	0.21 cal/g/°C
Specific resistivity	1.8×10^{13} ohms/cm
Vapor pressure @30°C	28 mm
Viscosity @20°C	0.90 centipoise
Water content	0.008% by wt
Weight per gallon @25°C	13.46 lb

TETRACHLOROETHYLENE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
2.6	Acetamide	120.5
38.5	Acetic acid	107.4
46	Allyl alcohol	93.4
52	1-Bromo-3-Methylbutane	119.3
29	Butanol	109.0
24.3	2-Chloroethanol	110.0
26	Diethyl carbonate	118.6
51.5	Epichlorohydrin	110.1
63	Ethanol	76.8
43	Ethyl butyrate	119.5
6	Glycol	119.1
20	Isoamyl alcohol	116.1
35	Isoamyl formate	117.9
40	Isobutanol	103.1
70	Isopropanol	81.7
3	Isobutyric acid	120.5
53	Isobutyl acetate	115.5
35	Isobutyl ether	119.5
55	Isopropyl isobutyrate	119.0

24.5	2-Methoxyethanol	109.7
42	Isobutyl nitrate	117.0
52	4-Methyl-2-Pentanone	113.9
32	Paraldehyde	118.8
48	Propanol	94.1
8.5	Propionic acid	119.2
19.5	Pyrrol	113.4
43	1,1,2-Trichloroethane	112.0
52	Triethyl borate	117.5

SOLVENT EDM

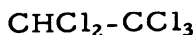
Solvent EDM consists of 75 per cent ethylene dichloride and 25 per cent carbon tetrachloride, by volume. This excellent solvent for oils, waxes, gums, and tars, is not flammable under ordinary conditions. It is used as an active solvent component in industrial cleaning compounds, type cleaners, spotting solvents, and other specialty products. It is also applied in cleaning textiles and in removing oil and grease from machinery.

"OXYFUME" FUMIGANT

"Oxyfume" fumigant is a combination of 81.2 per cent ethylene dichloride and 18.8 per cent ethylene oxide, by weight. This special fumigant mixture is used to control the infestation of insects in dried fruit kept in bulk storage. It is considered to be effective on fruit stored either in air-tight rooms or under tarpaulins (29).

"CHLORASOL" FUMIGANT

"Chlorasol" fumigant is a mixture of 70.3 per cent ethylene dichloride and 29.7 per cent carbon tetrachloride, by weight. It is an effective fumigant for meal, grain, and clothes moths; grain weevils; grain, flour, and carpet beetles; the rice weevil; and book lice, etc. It is nonflammable under ordinary conditions and evaporates quickly at room temperatures of 70° or higher. An increase is shown in the rate of evaporation and the depth of penetration as the temperature increases (29).

PENTACHLOROETHANE

Pentachloroethane is a heavy, colorless, nonflammable, toxic liquid, made by chlorinating tetrachloroethane or trichloroethylene. This high-boiling solvent is stable, in the absence of water. It is a good solvent for vegetable, mineral, and essential oils, for gum, resins such as dammar, elemi, mastic, sandarac, and for cellulose acetate and some types of cellulose ethers. Since its physical and chemical properties and solvent power are similar to the more toxic tetrachloroethane, it may be substituted for the latter in most industries. The solvent mixtures for cellulose acetate suggested by Lindsay, of which there are about 200 combinations, contain pentachloroethane.

PHYSICAL PROPERTIES

Acidity as HCl	0.001% by wt, max.
Boiling point @760 mm	161.9°C
Coefficient of cubical expansion Av./°C, liquid	0.000907
Color (Saybolt)	18 max.
Explosion limits	None
Flash point	Nonflammable
Free halogen	None
Freezing point	-22.0°C

Latent heat of vaporization @ B. P.	43.6 cal/g 78.4 Btu/lb
Nonvolatile matter	0.0007% by wt, max.
Refractive index	1.5035
Solubility in water @25°C	0.05 g/100 g
Solubility of water in solvent @20°C	0.24 g water/100 g
Specific gravity @20.4°C	1.678
Specific heat Liquid, 20°C	0.215 cal/g/°C
Vapor density (B. P. and 760 mm)	568 g/liter
Vapor pressure @30°C	6 mm
Viscosity liquid @20°C	2.45 centipoises
Weight per gallon @20°C	14.00 lb

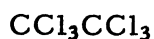
PENTACHLOROETHANE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
3	Acetamide	160.5
26	Butyric acid	156.8
97	Camphene	159.3
9.9	Chloroacetic acid	158.7
36	Cyclohexanol	157.9
28	Cyclohexanone	165.4
22.5	1,3-Dichloro-2-Propanol	159.7
32	Dimethyl oxalate	157.6
65	Ethyl lactate	153.5
50	2-Furaldehyde	155.2
15	Glycol	154.5
46	Hexyl alcohol	155.8
50	Isoamyl propionate	158.7
43	Isobutyric acid	152.9
9	Isovaleric acid	160.3
56	Mesitylene	166.0
97	Methylheptenone	173.3
9.5	Phenol	160.9
89	α -Pinene	155.6

HEXACHLOROETHANE

Perchloroethane

Carbon trichloride



Tetrachloroethylene dichloride

Hexachloroethane is a nonflammable, white to slightly yellow, crystalline compound, with a camphor-like odor. It is insoluble in water, but is soluble in ethyl alcohol, ethyl ether, and oils. It is used in the manufacture of synthetic organic chemicals and in smoke screen manufacture.

PHYSICAL PROPERTIES

Acidity as HCl	Less than 0.05%
Boiling point @ 760 mm	Sublimes @ 185°C
Latent heat of vaporization @ B. P.	46.4 cal/g 83.5 Btu/lb
Melting point in sealed tube	188.2°C
Nonvolatile matter	Less than 0.15%
Purity	98.0% min.
Specific gravity @ 20/4°C	2.091
Specific heat @ 25°C	0.174 cal/g/°C or Btu/lb/°F
Vapor density (B. P., 760 mm)	6.30 g/liter
Vapor pressure @ 30°C	2 mm
Water	0.2% by wt, max.

HEXACHLOROETHANE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
34	Aniline	176.8
12	Benzyl alcohol	182.0
30	p-Bromotoluene	183.5
25	Chloroacetic acid	171.2

28	o-Cresol	181.3
43	Diethyl oxalate	178.6
20	Diisobutyl carbonate	184.0
55	Dimethyl malonate	176.0
49.5	Ethyl acetoacetate	172.5
37	Isovaleric acid	172.6
30	Phenol	173.7
15	Trichloroacetic acid	181.0

ALLYL CHLORIDE

3-Chloropropene - 1

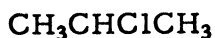


Allyl chloride is a water-white, volatile liquid with a mild odor. It is soluble in ethyl alcohol, ethyl ether, and carbon tetrachloride, but insoluble in water. It is used as a special solvent in organic synthesis of analogs of pyrethrins and in the manufacture of pharmaceuticals.

PHYSICAL PROPERTIES

Boiling point	45°C
Fire point	4°C
Flash point	4°C
Latent heat of vaporization	84.6 cal/g
Specific gravity @25/25°C	0.933
Specific heat	0.31 cal/g/°C
Refractive index @25°C	1.412
Viscosity @25°C	0.33 centipoise
Weight per gallon @25°C	7.8 lb

ISOPROPYL CHLORIDE



Isopropyl chloride is a clear, colorless liquid with an ethereal odor. It is miscible with alcohol and ether, but only slightly soluble in water. It is

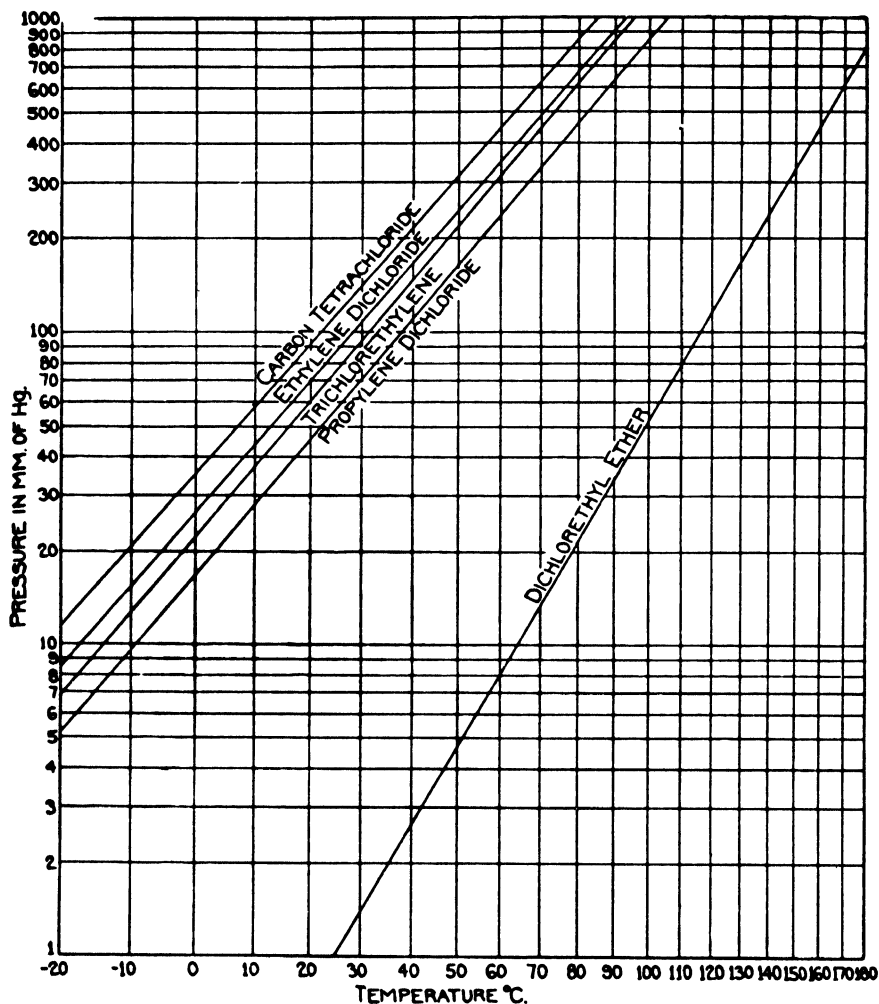


Fig. 15. Vapor pressure of various chlorinated solvents at different temperatures.

used as a special solvent in the manufacture of thymol and in organic synthesis.

PHYSICAL PROPERTIES

Boiling point	35.4°C
Freezing point	-117°C
Refractive index	1.3811
Solubility in water @12.5°C	0.344
Specific gravity @20/4°C	0.8590 g/100 g
Viscosity @22.5°C	0.2962 centipoise
Weight per gallon	7.5 lb

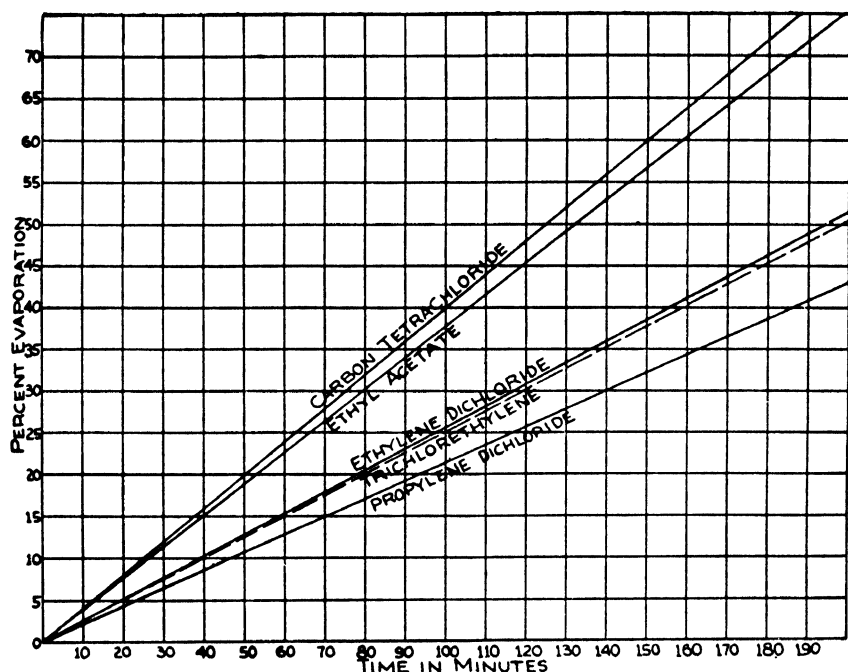


Fig. 16. Evaporation rate of ethyl acetate and various chlorinated solvents at room temperature.

PROPYLENE DICHLORIDE

1,2-Dichloropropane



Propylene chloride

Propylene dichloride is a stable, water-white liquid with a characteristic odor. Its flammability is low but it can be made nonflammable by adding 25 per cent, by volume, of carbon tetrachloride. Its odor and solvent properties resemble those of ethylene dichloride. It is soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride, and most organic solvents. It is a solvent for oils, fats, waxes, gums, resins, and some dyes. When an active solvent such as acetone is added, propylene dichloride becomes a solvent for cellulose esters and ethers. Because of its wide range of solvency, its low specific gravity, and its stability, it is a desirable solvent in many industries. It is used as an intermediate in the synthesis of amines and rubber chemicals, as an inert reaction medium for chlorination and sulfonation, as an ingredient in dry-cleaning fluids, scouring compounds, and spotting agents. It is also used as a soil fumigant and insecticide.

PHYSICAL PROPERTIES

Acidity as HCl	0.005% max.
Boiling point	95.9°C
Boiling range @ 760 mm	93-99°C
Coefficient of expansion per °C	0.001108-20°C 0.001153-55°C
Dielectric constant, 85.8 kilocycles	8.925 recip. ohms @ 26°
Explosive limits in air	Lower = 3.14% by vol. @ 25°C Upper = 14.5% by vol. @ 100°C
Flash point (ASTM O. C.)	21°C
Free halogen	None
Freezing point	-70°C
Ignition temperature in air	557°C

Latent heat of vaporization @ B. P.	72.2 cal/g
Nonvolatile matter	0.005 g/100 cc, max.
Refractive index	1.4418
Solubility in water @ 20°C	0.26% by wt
Solubility of water in solvent @ 20°C	0.07% by wt
Specific gravity @ 20/20°C	1.157-1.163
Specific heat Liquid, 20°C	0.31 cal/g/°C or Btu/lb/°F
Surface tension @ 25°C	31.4 dynes/cm
Vapor density (B. P., 760 mm)	3.72 g/liter
Vapor pressure @ 20°C	35.8 mm
Viscosity @ 20°C	0.00865 poise
Weight per gallon @ 20°C	9.65 lb

TRICHLOROPROPANE



1,2,3-Trichloropropane is now available in commercial quantities. It is considered to have high solvency for oils, fats, waxes, chlorinated rubber, and numerous natural and synthetic resins. Its low evaporation rate indicates use in paint and varnish removers and engine-cleaning compounds. It is reasonably nonflammable and will not ignite at any temperature below its boiling point.

PHYSICAL PROPERTIES

Analysis, % W	
Trichloropropane	97.0
Epichlorohydrin	1.5
Glycerol dichlorohydrin	1.5
Color, Pt-Co	15
Distillation range, IBP	150°C
90%	156.1°C
95%	156.1°C
DP	156.6°C

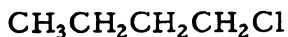
Flash point	165°F
Molecular weight	147.44
Refractive index	1.4832
Specific gravity @20/20°C	1.385

1, 2, 3-TRICHLOROPROPANE FORMS AZEOTROPES WITH

%		B. P. °C of Azeotrope
35	Camphene	152.9
30	2, 7-Dimethyloctane	155.5
15	α -Pinene	150.0

n-BUTYL CHLORIDE

1-Chlorobutane



Normal butyl chloride is a water-white liquid insoluble in water. It is soluble in methyl and ethyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acids, and hot paraffin and carnauba waxes, the latter two congealing when cooled. It is used as a solvent and in organic synthesis, particularly as a butylating agent for introducing the butyl group into different organic compounds. It is also used as an anthelmintic.

PHYSICAL PROPERTIES

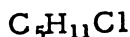
Acidity	0.01% max.
Boiling point @760 mm	78°C
Distillation range	Not less than 95% between 76.0-79.5°C
Flash point (O. C.)	20°F
Latent heat of vaporization @76.5°C	79.8 cal/g
Melting point	-123.1°C
Refractive index @20°C	1.4004

Solubility in water	Negligible
Specific gravity @20/4°C	0.884
Specific heat @20°C	0.451 cal/g
Surface tension @20°C	23.66 dynes/cm
Water content	None
Weight per gallon	7.37 lb

n-BUTYL CHLORIDE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
80	Acetone	55.8
1.9	n-Butyl alcohol	77.7
57	n-Butyl nitrite	76.5
35	Ethyl acetate	76.0
20.3	Ethyl alcohol	65.7
4	Isobutyl alcohol	77.7
62	Isobutyl nitrite	66.2
23	Isopropyl alcohol	70.8
29	Methyl alcohol	57.0
38	Methyl propionate	76.8
40	Methyl propyl ketone	77.0
16	Nitromethane	75.0
18	n-Propyl alcohol	74.8
38	n-Propyl formate	76.1
6.6	Water	68.1

MIXED AMYL CHLORIDES



This product is believed to be a mixture of all the monochlorides of normal and isopentane. This is a straw-to-purple colored liquid insoluble in water but soluble in methyl alcohol, ethyl ether, acetone, ethyl acetate, aromatic and aliphatic hydrocarbons,

fixed oils, mineral oil, oleic and hot stearic acids, and hot paraffin and carnauba waxes, the latter two congealing when cooled. The product may be used as a solvent, in rotogravure inks, and for soil fumigation when combined with the dichloropentanes, but its principal use is in the synthesis of amyl compounds.

PHYSICAL PROPERTIES

Acidity as HCl	0.03% max.
Amylene and pentane content	3.0% max.
Boiling point (approx.)	
1-Chloropentane	108.2°C
2-Chloropentane	96.7°C
3-Chloropentane	97.3°C
1-Chloro-2-methylbutane	99.9°C
4-Chloro-2-methylbutane	98.8°C
3-Chloro-2-methylbutane	93.0°C
2-Chloro-2-methylbutane	86.0°C
Distillation range	95% between 85-109°C
Evaporation rate @108°F:Minutes	
1.30	25%
1.67	50%
4.30	75%
6.58	100%
Flash point (O. C.)	34°F
Kauri-butanol value	71 cc
Solubility in water	Negligible
Specific gravity @20°C	0.88
Vapor pressure @20°	42.8 mm
Water azeotrope @77-82°C	90% C ₅ H ₁₁ Cl (approx.)
Weight per gallon	7.33 lb

n-AMYL CHLORIDE

1-Chloropentane CH₃CH₂CH₂CH₂CH₂Cl

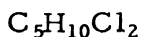
Normal amyl chloride is a colorless to straw-colored liquid with a sweet odor. It contains isomeric amyl chlorides and amylene as impurities.

It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, hot stearic acid, aromatic and aliphatic hydrocarbons, and hot paraffin and carnauba waxes which congeal on cooling.

PHYSICAL PROPERTIES

Acidity as HCl	0.025% max.
Amylene	1% max.
Boiling range	105-109°C
Distillation	95% between 104.9-108.9°C
Flash point	54°F
Other hydrocarbons	None
Polychlorides content	None
Solubility in water	Insoluble
Specific gravity @20/20°C	0.885
Weight per gallon	7.38 lb

DICHLOROPENTANES

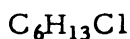


On standing, this liquid forms hydrochloric acid due to the instability of some of the isomers in the mixture. The distilled product is light yellow in color while the undistilled product is brown to black. It is insoluble in water, but is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acids, and hot paraffin and carnauba waxes, the latter two congealing when cooled. It dissolves oils, greases, unvulcanized rubber, and some resins and bituminous substances. It is used as a metal degreasant, as an ingredient in paints and varnish removers, as a solvent in varnish and nitrocellulose lacquers, in plastics, and for reclaiming rubber. It is also used as a soil fumigant. Its penetrating power is increased by mixing it with lubricating oils. In combination with 20 per cent carbon tetrachloride, a nonflammable mixture is formed.

PHYSICAL PROPERTIES

Acidity as HCl	0.025% max.
Average chlorine content	48%
Distillation	95% between 130-200°C
Evaporation rate @109°F:Minutes	
3.83	25%
8.00	50%
14.20	75%
90.00	100%
Flash point (O. C.)	97°F
Heat of vaporization	68.5 cal/g
Kauri-butanol value	67 cc
Solubility in water	Negligible
Specific gravity @20°C	1.07-1.08
Specific heat	0.369 cal/g
Surface tension @25°C	31.8 dynes/cm
Viscosity @25°C	0.016 poise
Water azeotrope @80-97°C	66% C ₅ H ₁₀ Cl ₂ (approx.)
Water content	None
Weight per gallon	8.94 lb

n-HEXYL CHLORIDE

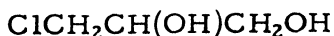


n-Hexyl chloride is a water-white liquid with a sweet odor. It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, and aromatic and aliphatic hydrocarbons. It is also soluble in hot paraffin and carnauba wax. but they congeal on cooling. It is insoluble in water.

PHYSICAL PROPERTIES

Boiling range	133-135°C
Flash point	95°F
Specific gravity @20/20°C	0.877

MONOCHLOROHYDRIN



Monochlorohydrin is a colorless, hygroscopic, and unstable liquid made by passing hydrochloric acid gas into glycerol containing 2 per cent acetic acid. The commercial grade is a mixture of the two isomers, alpha and beta, of which alpha is in greater proportion. Monochlorohydrin is a solvent for acetylcellulose and alkyd resins, and partially dissolves ester gum, benzyl abietate, shellac, and mastic. It is miscible with water and a number of organic solvents, but will not mix with oil and hydrocarbons. A mixture of 40 per cent monochlorohydrin and 60 per cent water will dissolve cellulose acetate. It is used also as an intermediate in organic syntheses.

PHYSICAL PROPERTIES

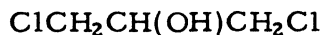
Boiling point	213°C
Boiling range	213-228°C (decomposes)
Specific gravity @18°C	1.326

DICHLOROHYDRIN

Glycerol dichlorohydrin

Dichloroisopropyl alcohol

1,3-dichloropropanol-2



α -propenyldichlorohydrin

Dichlorohydrin is a colorless, slightly viscous, nonflammable, unstable liquid with a faint chloroform-like odor. In commerce it is a mixture of the two isomers, 1,3-dichloro-2-hydroxypropane and 1,2-dichloro-3-hydroxypropane, of which the former predominates. It is a solvent for cellulose acetate, ethyl cellulose, some cellulose nitrates, benzyl abi-

etate, soft copal, copal ester, dammar, elemi, coumarone resin, ester gum, glyptal resins, manila, mastic, shellac, etc. The mixture of dichlorohydrins is miscible with vegetable oils and most organic solvents, and is soluble in water to the extent of 10 per cent. It is used as a solvent for resins and cellulose lacquers, in celluloid cements, as a binder for water colors, and as an intermediate in organic syntheses.

PHYSICAL PROPERTIES

Boiling point	(1,3-) 174°C (1,2-) 183°C
Boiling range	174-176°C (95%)
Flash point	74°C
Refractive index	1.47-1.48
Specific gravity	1.36-1.39
Vapor pressure	7 mm

1,3-DICHLORO-2-PROPANOL FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
91	Bromobenzene	155.5
39	o-Bromotoluene	170.5
32	p-Bromotoluene	172.8
62	Camphene	152.8
43	α-Chlorotoluene	168.9
85	o-Chlorotoluene	158.0
78	p-Chlorotoluene	160.0
45	Cymene	165.5
55	p-Dichlorobenzene	162.2
62	2,7-Dimethylactane	155.0
85	Dimethyl oxalate	162.0
33.5	Indene	173.5
30	Iodobenzene	173.0
10	Isoamyl butyrate	178.6

52	Isoamyl ether	165.9
43	d-Limonene	166.8
50	Mesitylene	156.0
41	p-Methylanisole	173.1
35	Methylheptenone	178.5
57	α -Phellandrene	163.0
63.5	α -Pinene	150.4
63	Pseudocumene	164.4
85	Styrene	142.5
38	α -Terpinolene	166.8
40	Thymene	166.5

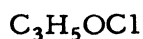
1,2-DICHLORO-3-PROPANOL FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
55	o-Bromotoluene	171.6
75	Camphene	156.0
60	α -Chlorotoluene	171.0
68	Indene	160.0
60	α -Limonene	169.3
43	2-Octanol	172.5
80	α -Pinene	153.0
50	Thymene	170.8

EPICHLOROHYDRIN

Chloropropylene oxide

1-Chloro-2,3-epoxypropane



Epichlorohydrin is a colorless, mobile, highly volatile liquid with a characteristic chloroform-like odor. Because of its chlorine atom and epoxide ring, it is highly reactive. It is miscible with lower aliphatic alcohols, ethers, esters, ketones, aliphatic halogenated hydrocarbons, fixed oils, carbon tetrachloride, benzene, gasoline, and aliphatic halogen derivatives. It is immiscible with water, glycerin,

and petroleum hydrocarbons. It is a powerful solvent for many types of cellulose esters and ethers, synthetic and natural resins, and gums. It is a solvent for ester gum, rosin, and cellulose acetate, and when mixed with butyl acetate, it becomes compatible with cellulose nitrate. It is used largely as an intermediate in the synthesis of pharmaceuticals, resins, etc. (30).

PHYSICAL PROPERTIES

Boiling point @ 760 mm	116.11 °C
Boiling range (ASTM gasoline still) @ 736 mm	90% between 114-118 °C
Coefficient of expansion @ 68 °F	0.000577/°F
Dielectric constant ($\lambda = 60$ cm)	20.8 @ 21.5 °C
dt/dp @ the boiling point	0.044 deg/mm
Flash point (Tag O. C.)	105 °F
Freezing point	-57.2 °C
Heat of combustion	4524.4 cal/g
Latent heat of vaporization (calc.)	9060 cal/mole, @ B.P.
Molecular weight	92.53
Refractive index N_D^{20}	1.43805
Solubility in water @ 20 °C	6.48% by wt
Solubility of water in solvent @ 20 °C	1.09% by wt
Specific conductance @ 25 °C	34×10^{-9} ohms ⁻¹ cm ⁻¹
Specific gravity @ 20/4 °C	1.1807
Specific gravity @ 20/20 °C	1.1828
Vapor pressure @ 20 °C	13 mm Hg
Weight per gallon @ 68 °F	9.85 lb

EPICHLOROHYDRIN FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
34.5	Acetic acid	115.1
78	Allyl alcohol	95.8
70	tert-Amyl alcohol	100.1

83	1-Bromo-2-Chloroethane	103.5
48	1-Bromo-3-Methylbutane	110.1
43	Butanol	112.0
75	2, 5-Dimethylhexane	107.0
8	1-Iodobutane	115.0
25	Ethyl butyrate	115.8
19	Isoamyl alcohol	115.4
60.5	Isobutanol	105.0
50	Isobutyl acetate	115.3
55	Methyl isovalerate	115.0
20	n-Octane	114.5
77	Propanol	96.0
53	1-Iodo-2-Methylpropane	111.0
48.5	Tetrachloroethylene	110.1
71	Toluene	108.4

GLYCEROL ALPHA-MONOCHLOROHYDRIN



Glycerol alpha-monochlorohydrin is a water-white to light brown, viscous liquid with very little odor. It is soluble in water, ethyl and methyl alcohols, glycerol, ethyl ether, ethyl acetate, acetone, fixed oils, and oleic acid. It is insoluble in benzene, gasoline, carbon tetrachloride, aromatic and aliphatic hydrocarbons, mineral oil, ester gum, dammar gum, carnauba wax, paraffin wax, rosin, and linseed oil. It is a solvent for cellulose acetate and nitrocellulose, when mixed with a butyl acetate solution. Its solvent properties are due to the hydroxyl and chloride groups in the molecule. It is used principally in organic synthesis.

PHYSICAL PROPERTIES

Boiling point	213°C
Boiling range (ASTM)	90% between 136-142°C @ 40 mm
Flash point (O. C.)	280°F
Refractive index @ 25°C	1.4781
Solubility in water	100%
Specific gravity @ 20/4°C	1.320
Weight per gallon	10.98 lb

PROPYLENE CHLOROHYDRIN

Chloroisopropyl alcohol



Propylene chlorohydrin is a colorless liquid with a mild odor; it is freely soluble in water. It is largely used in organic syntheses, for the purpose of introducing the hydroxypropyl group.

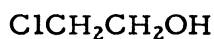
PHYSICAL PROPERTIES

Acidity as HCl	0.02% by wt
Absolute viscosity @ 20°C	4.7 centipoises
Apparent specific gravity @ 20/20°C	1.1128
Boiling point @ 760 mm Hg	127.4°C
@ 50 mm Hg	59°C
@ 10 mm Hg	31°C
Coefficient of expansion @ 55°C	0.00097
Constant-boiling mixture @ 760 mm:	
Chlorhydrin approx. 46%	
Water 54%	B. P. 95.4°C
Flash point (Cleveland O. C.)	125°F
Molecular weight	94.54
Solubility in water	Miscible in all proportions
Vapor pressure @ 20°C	4.9 mm Hg
Weight per gallon @ 20°C	9.29 lb

ETHYLENE CHLOROHYDRIN

Glycol chlorohydrin

2-Chlorethyl alcohol

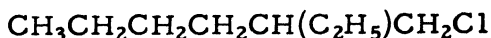


Ethylene chlorohydrin is a colorless, highly refractive, and toxic liquid with an ethereal odor. It is made by the action of chlorine water on ethylene, and the commercial product is either in the anhydrous form or as a 38 per cent aqueous solution. This solvent is miscible with water, ethyl alcohol, and benzene. It has the unusual property of dissolving cellulose acetate while tolerating the addition of water. It becomes a solvent for ethyl cellulose, when admixed with methyl alcohol. Ethylene chlorohydrin, as well as propylene or butylene chlorohydrin, become powerful solvent mixtures for cellulose acetate when mixed with water or water and alcohol. Ethylene chlorohydrin is used in the synthesis of such substances as phenylethyl alcohol, novocaine, and indigo; it is also used for the introduction of the hydroxyethyl group. The 38 per cent aqueous solution is used to activate the sprouting of dormant potatoes.

PHYSICAL PROPERTIES

Absolute viscosity @ 20°C	3.4 centipoises
Apparent specific gravity @ 20/20°C	1.2040
Boiling point @ 760 mm Hg	128.7°C
@ 50 mm Hg	60°C
@ 10 mm Hg	29°C
Coefficient of expansion @ 55°C	0.00092
Flash point (Cleveland O. C.)	140°F
Freezing point	-62.6°C
Molecular weight	80.52
Pounds per gallon @ 20°C	10.03
Solubility in water @ 20°C	Complete
Solubility of water in solvent @ 20°C	Complete
Vapor pressure @ 20°C	4.9 mm Hg

2-ETHYLHEXYL CHLORIDE



2-Ethylhexyl chloride is a water-white liquid with a mild odor similar to other chlorinated hydrocarbons. It is a good solvent for oils, fats, and waxes, and because of its relatively high boiling point, it may serve in the extraction of higher-melting solid fats and waxes. It is used in the production of surface-active agents of the alkyl-aryl acid type. It is also used as an alkylating agent for the introduction of 2-ethylhexyl groups. Such derivatives are found to be of interest in petroleum additives, extraction processes, and as plasticizers.

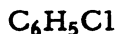
PHYSICAL PROPERTIES

Average weight @20°C	7.33 lb/gal
Boiling point @760 mm Hg	172.9°C
Flash point (O. C.)	140°F
Molecular weight	148.67
Solubility in water @20°C	0.1% by wt
Solubility of water in solvent @20°C	0.1% by wt
Specific gravity @20/20°C	0.8833
Vapor pressure @20°C	1.3 mm Hg

MONOCHLOROBENZENE

Chlorobenzene

Phenyl chloride



Monochlorobenzol

Monochlorobenzene is a flammable, mobile, colorless, volatile liquid, with an almond-like odor. It is considered less toxic than benzene. This solvent is made by the chlorination of benzene in the presence of a chlorine carrier. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, carbon

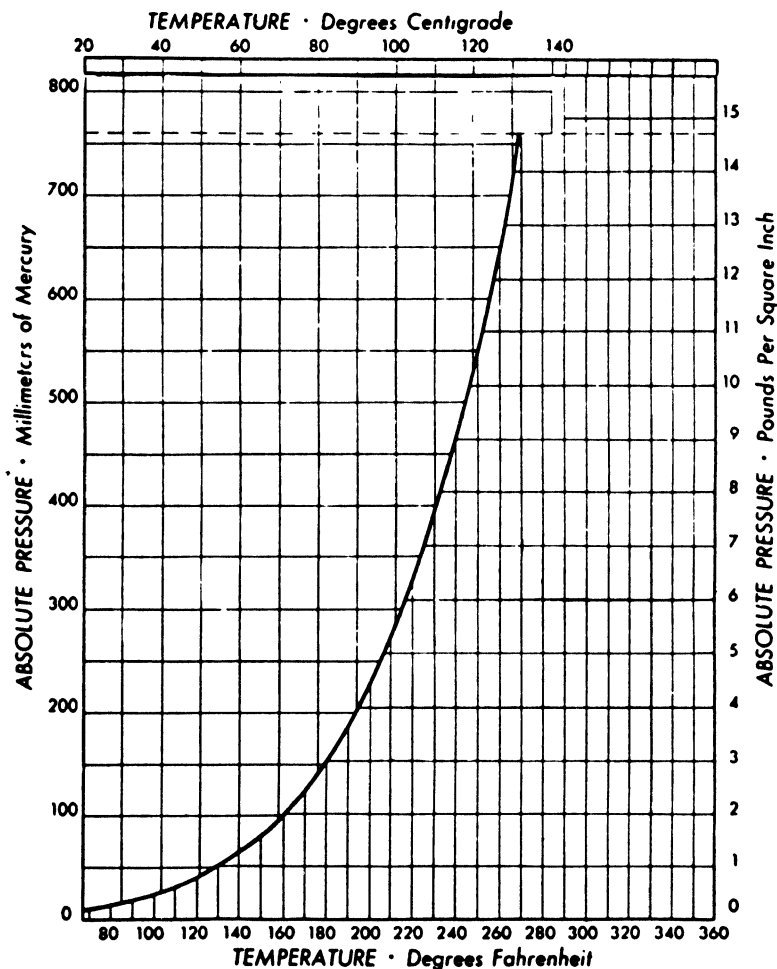


Fig. 17. Vapor pressures of monochlorobenzene.

tetrachloride, and most organic solvents. It will dissolve ethyl cellulose, many natural and synthetic resins such as rosin, dammar, soft copal, vinyl resins, "Bakelite," acetylcellulose. In common with other halogenated hydrocarbons, the solvent power of chlorobenzene is increased by adding amyl, butyl, ethyl or methyl alcohol, or their acetate esters. It is added to lacquers because of its unique property of

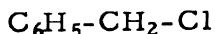
producing a crackle or matte effect. It is a solvent for removing paint or tars, etc., and is used in the manufacture of chemicals such as aniline, phenol, picric acid, poison gases, dyes, drugs, synthetic perfumes, and insecticides; it is also used in other organic syntheses.

PHYSICAL PROPERTIES

Boiling point @ 760 mm	131.6°C
Dielectric constant, 1000 cycle	5.53
Electrical conductivity @ 0°C	10^{-9} recip./ohm
Fire point	36°C
Flash point	27°C
Freezing point	-45°C
Latent heat of vaporization @ B. P.	77.6 cal/g
Refractive index @ 15°C	1.52748
Solubility in water @ 30°C	0.049% by wt
Specific gravity @ 15/4°C	1.1117
Specific heat	0.30 cal/g/°C
Specific resistivity	7.8×10^9 ohms/cm
Surface tension (C. G. S. units)	33.08
Vapor pressure @ 20°C	8.71 mm
Viscosity @ 15°C	0.00844 cgs unit
Weight per gallon @ 25°C	9.19 lb

BENZYL CHLORIDE

α -Chlorotoluene



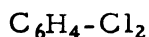
Benzyl chloride is a clear, colorless to pale-yellow liquid with a sharp and pungent odor. It is a lachrimator, and its toxic vapors should not be breathed or come in contact with the skin. It is miscible with alcohols, ethers, and halogenated hydrocarbons, but is insoluble in water. Because of its reactivity, it finds use in the synthesis of dyestuffs, resins, germicides, pharmaceuticals, synthetic rubber, rubber accelerators, plasticizers, perfume bases, wetting agents, and gasoline gum inhibitors (56).

PHYSICAL PROPERTIES

Distillation range	Not more than 2° including 179.4°C
Freezing point	-43°C
Molecular weight	126.58
Refractive index N_D^{25}	1.5365
Specific gravity @15.5°/15.5°C	1.107
Weight per gallon @15.5°C	9.23 lb

o-DICHLOROBENZENE

1,2-Dichlorobenzene



"Orthene"

o-Dichlorobenzene is a stable, heavy, colorless, volatile liquid with an aromatic odor. It is considered nonflammable but will burn when ignited. This solvent is a mixture composed principally of the ortho compound and varying amounts of para and meta isomers. It is insoluble in water, but soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride, and most common solvents. It is a solvent for oxides of nonferrous metals, waxes, tars, unvulcanized rubber, greases, oils, asphalts, sulfur, organic sulfur derivatives, natural and synthetic gums and resins, and acetylcellulose, etc.

It is added to lacquers and varnishes for its solvency, penetration, slow evaporation and its ability to impart easy working qualities and freedom from orange peel. It is used for degreasing metals, leather, hides, automobiles, and as an ingredient in metal polish. It is a wax solvent, an anti-skinning agent in varnishes, a termite exterminator, repellent and wood preservative. It is employed as a spotting agent, tar solvent, fungicide, preservative, and fumigant, and in the organic synthesis of dyes and drugs. It is also used in the removal of sulfur from illuminating gases.

o-Dichlorobenzene is used as a solvent for special cleaning problems in the vapor phase, as a liquid hot dip, or as a liquid cold dip. The basic formula applied for these uses is as follows:

	% by weight	
	Maximum	Minimum
Orthodichlorobenzene	--	53
Cresylic acid (100% acid basis)	25	23
Water	5 (by volume)	--
Potassium oleate (anhydrous basis)	12	10
Inhibitors and other materials	5	--

Many modifications are used.

PHYSICAL PROPERTIES

	Purified	Technical
Boiling point	180.2°C	179.6°C
Boiling range (within)	3.0°C	4.0°C
Dielectric constant 1000 cycles	9.82	
Electrical conductivity @0°C	10 ⁻⁹ recip. ohm	
Fire point	103°C	103°C
Flash point	68°C	68°C
Freezing point	-18.3°C	-22.5°C
Heat of combustion	671.8 kg cal/mol.	
Heat of fusion	88 joules/g	
Impurities (p-dichlorobenzene, trichlorobenzene)	Not over 4%	Not over 12%
Latent heat of vaporization @ B. P.		65 cal/g at.
Refractive index @22°C		1.5518
Solubility in water @25°C		Less than 0.01%
Specific gravity @20/4°C		1.3048

Specific heat	0.271 cal/g/°C
Specific resistivity	2.0×10^8 ohms/cm
Weight per gallon @25°C	10.85 lb

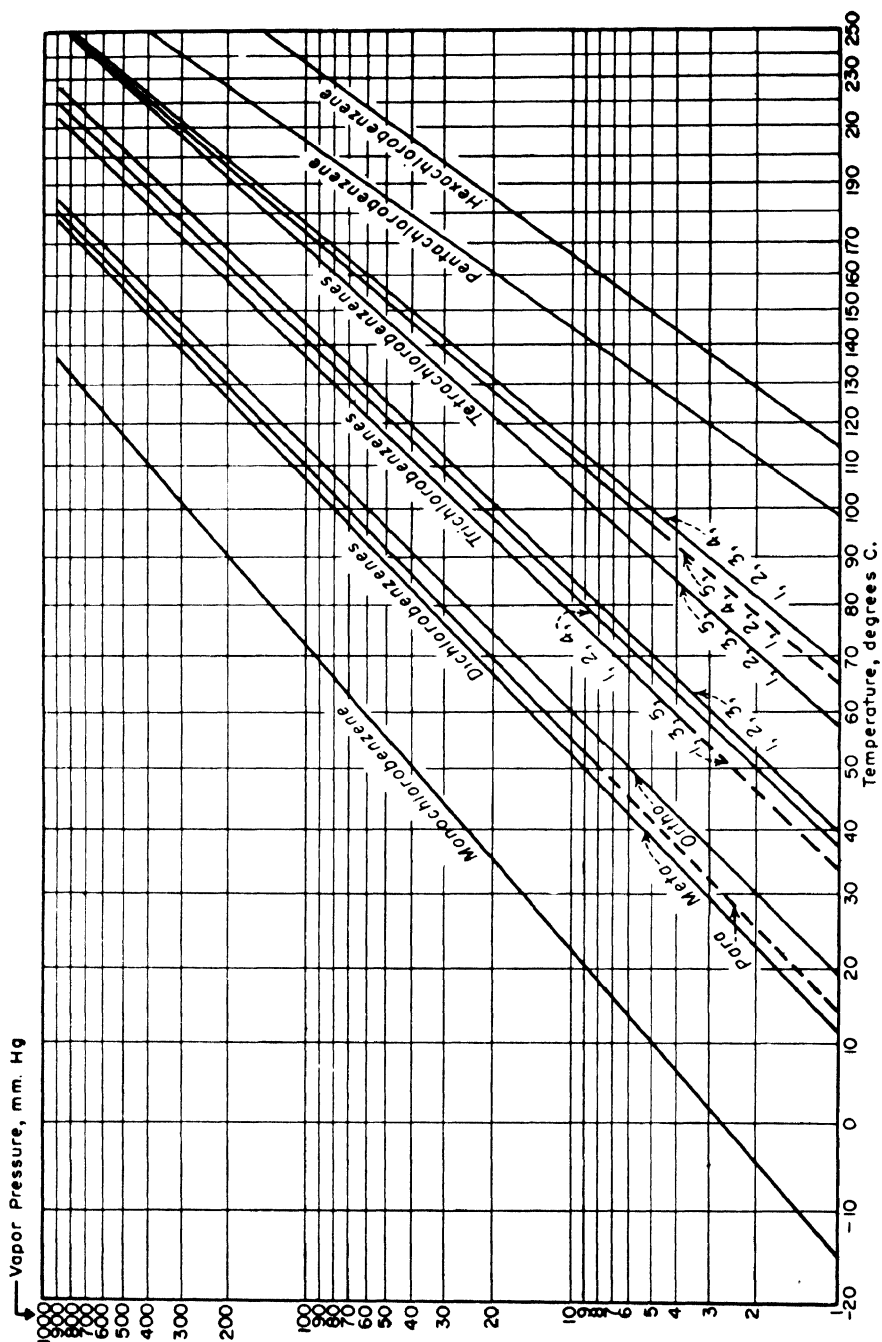
p-DICHLOROBENZENE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
20	Cineole	173.5
33.5	Cyclohexanol	153.6
37	2-Ethoxyethyl acetate	155.5
34	n-Hexyl alcohol	151.6
46	Camphene	155.0
63.5	Isoamyl ether	172.4
27	Isoamyl propionate	155.2
14	d-Limonene	174.2
50	α -Pinene	153.4
2	Phenol	156.0
43	Propyl isovalerate	154.5

MONOCHLOROTOLUENE



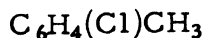
The technical grade of this solvent is a mixture of the ortho and para derivatives. It is a clear, colorless liquid, with an odor resembling monochlorobenzene. It is freely miscible with acetone, benzol, butanol, carbon tetrachloride, diethyl ether, ethylene dichloride, linseed oil, methanol, petroleum ether, and "Solvesso No. 2;" it is insoluble in water. It is a solvent for rubber and synthetic resins and is used in the manufacture of rubber accelerators and in organic synthesis.



PHYSICAL PROPERTIES

	Ortho	Para
Boiling point	159.4°C	162.5°C
Coefficient of cubical expansion @ 30°C		0.00092
Distillation range		
Start	158.3°C min.	
100%	165.1°C max.	
Flash point	46°C	
Freezing point	-34°C	7.5°C
Latent heat of vaporization		77 cal/g
Purity	60% approx.	40% approx.
Solubility of water @ 25°C		0.037 g/100 g
Solubility of water in solvent @ 25°C		0.014 g/100 g
Refractive index @ 20°C	1.5238	1.5199
Specific gravity @ 20/4°C	1.0817	1.0697
Surface tension @ 25°C		32.9 dynes/cm
Vapor pressure @ 100°C		132 mm
Viscosity @ 100°F	{ 0.707 centistoke { 0.747 centipoise { 0.328 centistoke { 0.327 centipoise	
@ 210°F		
Weight per gallon @ 25°C		

ortho-CHLOROTOLUENE



ortho-Chlorotoluene is a clear, practically colorless liquid, the vapors of which are toxic. It is soluble in methanol, absolute ethanol, 95 per cent ethanol, n-butanol, ethyl ether, amyl ether, methyl ethyl ketone, methyl amyl ketone, acetone, diacetone, butyl acetate, heptane, ethylene dichloride, and toluene, and insoluble in water. It is used as an intermediate for the preparation of dyestuffs, rubber

chemicals, pharmaceuticals, and other organic chemicals, as a special solvent, and as a carrier in dyeing synthetic fibers.

PHYSICAL PROPERTIES

Acidity as acetic acid	Nil
Boiling point @ 760 mm Hg	159.3°C
@ 50 mm Hg	77.0°C
@ 10 mm Hg	43.2°C
Congealing point	-30°C
Distillation range @ 760 mm Hg	159-160°C
Flash point (Cleveland O. C.)	136°F
Freezing point	-36°C (approx.)
Moisture content	Nil
Molecular weight	126.58
Pounds per gallon	8.95
Purity	99% min.
Refractive index N_{22}^D	1.5231
Side chain chlorine	None
Specific gravity @ 25/25°C	1.078 min. - 1.082 max.
Vapor pressure @ 94.7°C	100 mm Hg

3, 4-DICHLOROTOLUENE



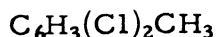
3, 4-Dichlorotoluene is a high-boiling, colorless to pale-yellow liquid, the vapors of which are toxic. It is soluble in alcohol, ether, ketones, and toluene, but insoluble in water. It is used as an intermediate in the preparation of dyestuffs, rubber chemicals, pharmaceuticals, as a special solvent, and as a carrier in dyeing synthetic fibers.

PHYSICAL PROPERTIES

Acidity as acetic acid, % by wt	Nil
Boiling point @ 760 mm Hg	209.0°C
@ 50 mm	120°C
@ 10 mm	83°C

Congealing point	-15°C
Distillation range @ 760 mm Hg	207-212°C
Fire point (Cleveland O. C.)	392°F
Flash point (Cleveland O. C.)	205°F
Moisture content	Nil
Molecular weight	161.04
Pounds per gallon	10.4
Purity	98.0%
Refractive index N_{22}^D	1.5490
Specific gravity @ 25/25°C	1.251 min. 1.255 max.
Surface tension DuNouy @ 25°C	39.18 dynes/cm
Vapor pressure @ 140°C	100 mm Hg

2, 4-DICHLOROTOLUENE



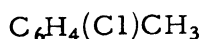
2,4-Dichlorotoluene is a high-boiling, colorless to pale-yellow liquid, the vapors of which are toxic. It is soluble in alcohol, ether, ketones, and toluene, but insoluble in water. It is used as an intermediate in the preparation of dyestuffs, rubber chemicals, pharmaceuticals, as a special solvent, and as a carrier in dyeing synthetic fibers.

PHYSICAL PROPERTIES

Acidity as acetic acid	Nil
Boiling point @ 760 mm Hg	200.5°C
@ 50 mm Hg	113.0°C
@ 10 mm Hg	77.0°C
Congealing point	-13°C
Distillation Range @ 760 mm Hg	199-202°C
Fire point (Cleveland O. C.)	383°F
Flash point (Cleveland O. C.)	199°F
Moisture content	Nil

Molecular weight	161.04
Pounds per gallon	10.34
Purity	99.0%
Refractive index N_{22}^D	1.5480
Side chain chlorine	None
Specific gravity @ 25/25°C	1.247 min. - 1.251 max.
Surface tension, DuNouy @ 25°C	38.29 dynes/cm
Vapor pressure @ 130°C	100 mm Hg

para-CHLOROTOLUENE



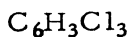
para-Chlorotoluene is a clear, practically colorless liquid, the vapors of which are toxic. It is soluble at 25°C in methanol, absolute ethanol, 95 per cent ethanol, n-butanol, ethyl ether, amyl ether, methyl ethyl ketone, methyl amyl ketone, acetone, diacetone, butyl acetate, heptane, ethylene dichloride, and toluene. It is used as an intermediate in the manufacture of dyestuffs, pharmaceuticals, rubber chemicals, and other organic chemicals, as a special solvent, and as a carrier in dyeing synthetic fibers.

PHYSICAL PROPERTIES

Acidity as acetic acid	Nil
Boiling point @ 760 mm Hg	162.3°C
@ 50 mm Hg	78.4°C
@ 10 mm Hg	43.8°C
Congealing point	6.8°C
Distillation range @ 760 mm Hg	162-166°C
Flash point (Cleveland O. C.)	140°F
Moisture content	Nil
Molecular weight	126.59
Pounds per gallon	8.85
Purity	98.0%
Refractive index N_{22}^D	1.5184

Side chain chlorine	None
Solidifies	Below 45°F
Specific gravity @25/25°C	1.067 min. - 1.071 max.
Surface tension (in air) DuNouy @25°C	34.60 dynes/cm
Vapor pressure @96.6°C	100 mm Hg

TRICHLOROBENZENE



Trichlorobenzene, a mixture of the isomers 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes, has an odor much like o-dichlorobenzene; it is volatile with steam and insoluble in water. Trichlorobenzene is fully miscible with: benzene, toluene, petroleum ether, "Solvesso 100," Stoddard Solvent, Petroleum Solvent 140 F, diethyl ether, carbon tetrachloride, chloroform, ethylene dichloride, perchloroethylene, trichloroethylene, cresylic acid, ethyl acetate, amyl acetate, dimethyl phthalate, linseed oil, acetone, methyl ethyl ketone, 100 per cent ethanol, n-butanol, dimethyl "Cellosolve," nitrobenzene, furfural, "Vaseline," and "Cosmoline." Trichlorobenzene is used as a solvent in oil-soluble dyes and for degreasing metals, as a dielectric fluid, as an addition agent to some lubricating oils, as a crystallizing medium, in insecticide compositions, for termite extermination, and as an intermediate.

PHYSICAL PROPERTIES

Boiling point @760 mm	213.6°C
Boiling range	5°C
Coefficient of cubical expansion @30°C	0.00086
Color (Saybolt)	20 max.
Dielectric constant, 1000 cycles	4.93
Dielectric strength (0.1" gap)	30,000 volts
Fire point (Cleveland O. C.)	None
Flash point (Cleveland O. C.)	210°F

Freezing point	16.4°C
Latent heat of vaporization	58.2 cal/g @ B. P.
Pour point	Below 10°C
Refractive index @20°C	1.5671
Solubility of water in trichlor @25°C	0.22 g/100 g
Solubility of trichlor in water @25°C	0.0025 g/100 g
Specific gravity @25/25°C	1.460
Specific heat	0.20 cal/g/°C
Specific resistivity	2.9×10^9 ohms/cm
Surface tension @25°C	38.9 dynes/cm
Vapor pressure @100°C	23 mm
Viscosity @100°F	$\left\{ \begin{array}{l} 1.100 \text{ centistokes} \\ 1.579 \text{ centipoises} \\ 0.549 \text{ centistoke} \\ 0.746 \text{ centipoise} \end{array} \right.$
@210°F	
Weight per gallon @25°C	

1, 2, 3-
TRICHLOROBENZENE1, 2, 4-
TRICHLOROBENZENE1, 3, 5-
TRICHLOROBENZENE

Synonym:	vic-Trichloro- benzene	uns-Trichloro- benzene	sym-Trichloro- benzene
Physical state	White crystals	Colorless liquid	White crystals
Boiling point @ 760 mm	221°C (429.8°F)	213°C (415.4°F)	208.5°C (407.3°F)
Density: 25/25°C	1.69 (solid)	1.451 (liquid)	
Flash point (Tag C. C.)	113°C (235.4°F)	110°C (230.0°F)	107°C (224.6°F)
Index (D_D^{19}) of Refraction:	1.5776	1.5732	1.5662

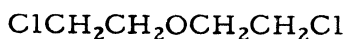
1, 3, 5-TRICHLOROBENZENE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
50	Camphor	210.5
43	Caproic acid	204.0
60	m-Cresol	200.5

40	p-Cresol	200.2
35	N-Ethylaniline	203.0
	Menthone	209.5
95	Phenol	181.3
	p-Toluidine	199.0

DICHLOROETHYL ETHER

2,2'-Dichloroethyl ether



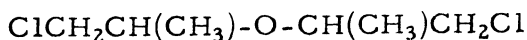
sym or β,β' -Dichloroethyl ether

Dichloroethyl ether is a colorless, stable, non-corrosive liquid, with an odor much like ethylene dichloride. It is insoluble in hydrocarbons, but soluble in most organic solvents. It is an active solvent for oils, fats, waxes, gums, tars, natural and synthetic resins, soaps, and ethyl cellulose. When mixed with an alcohol, it dissolves many types of cellulose esters and ethers, resulting from the combined action of the ethyl ether and ethylene dichloride groups in the molecule. In general, this solvent can replace ethylene dichloride, particularly in processes where high temperatures are required. It is used in paint and varnish removers, in spotting agents, and in cleaning solutions. Having a detergent action, it can be used to assist soap solutions in such textile processes as kier boiling, and scouring for the removal of paint, tar, oil, and grease spots. It is used in the textile industry as a softening and conditioning agent, as a substitute for caustic alkalies in kier boiling, in peroxide bleaching for penetration, in desizing, and as an aid in mercerizing. It is also employed as a selective solvent in the manufacture of high-grade lubricating oils from crude oils.

PHYSICAL PROPERTIES

Acidity as HCl	0.005% max.
Apparent ignition temperature in air	396°C
Boiling point	178°C
Boiling range @760 mm	Not more than 5% distills below 173°C Not less than 95% distills below 179°C
Color (500 mm tube)	Not more than 2 yellow Lovibond
Ethylene dichloride	1.0% max.
Flash point (C. C.)	55°C
Latent heat of vaporization @178°C	64.1 cal/g
Refractive index @20°C	1.457
Specific gravity @20/20°C	1.219-1.224
Specific heat @20-30°C	0.369 cal
Surface tension @25°C	41.8 dynes/ sq cm
Vapor pressure @20°C	1.2 mm
Viscosity @25°C	2.0653 centipoises
Weight per gallon @20°C	10.17 lb

DICHLORODIISOPROPYL ETHER

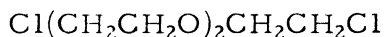


This compound is a colorless liquid with a mild odor; its properties are very similar to those of dichloroethyl ether. It is miscible with practically all oils, and with most organic solvents. It is a good solvent for fats, waxes, greases, and hydrocarbons, and is used as a high-boiling solvent, as an extractant, and in organic synthesis. It may also be used as a spotting agent, in cleaning solutions, and in paint and varnish removers.

PHYSICAL PROPERTIES

Acidity as HCl	0.01% by wt, max.
Boiling point @ 760 mm	187.3°C
Boiling range @ 760 mm	Not more than 5% distills below 180°C Not less than 95% distills below 190°C
Color (Pt-Co scale)	25 max.
Flash point (O. C.)	185°F
Solubility in water @ 20°C	0.17% by wt
Solubility of water in solvent @ 20°C	0.11% by wt
Specific gravity @ 20/20°C	1.1122
Vapor pressure @ 20°C	0.85 mm
Weight per gallon @ 20°C	9.26 lb

TRIGLYCOL DICHLORIDE



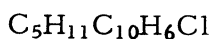
This solvent is a colorless liquid with a mild odor. It is miscible with practically all oils and with most organic solvents. It is a good solvent for fats, waxes, greases, and hydrocarbons, and is used as a high-boiling solvent, extractant, and in organic synthesis. It also has use as a spotting agent, in cleaning solutions, and in paint and varnish removers.

PHYSICAL PROPERTIES

Acidity as HCl	0.01% by wt, max.
Boiling point @ 760 mm	241.3°C
Boiling range @ 760 mm	Not more than 5% distills below 235°C Not less than 95% distills below 242°C
Color (Pt-Co scale)	25 max.
Dryness @ 20°C	Miscible with 19 vol. 60° Bé gasoline

Flash point (O. C.)	250°F
Solubility in water @20°C	1.89% by wt
Solubility of water in solvent @20°C	0.83% by wt
Specific gravity @20/20°C	1.1950-1.2000
Vapor pressure @20°C	0.06 mm
Weight per gallon @20°C	9.97 lb

MONOAMYL CHLORONAPHTHALENE

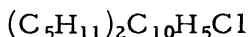


This solvent is a straw-colored liquid with a naphthalene-like odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, and aromatic and aliphatic hydrocarbons. It is also soluble in hot paraffin wax, hot carnauba wax, and hot stearic acid, but these congeal on cooling; it is insoluble in water and methyl alcohol.

PHYSICAL PROPERTIES

Flash point	295°F
Specific gravity @20/20°C	1.076

DIAMYL CHLORONAPHTHALENE



This solvent is an orange-colored liquid, with a naphthalene-like odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, and aromatic and aliphatic hydrocarbons. It is also soluble in hot paraffin wax, hot carnauba wax, and hot stearic acid, but these congeal on cooling; it is insoluble in water and methyl alcohol.

PHYSICAL PROPERTIES

Boiling range @760 mm	352-377°C
Flash point	330°F
Specific gravity @20/20°C	1.06

CHLORINATED NAPHTHALENES

The chlorinated naphthalenes, known by the registered trade-mark "Halowax," (52), are oils and wax-like solids. These compounds represent a group of crude and refined chlorinated naphthalene products ranging from low viscosity to hard crystalline solids. They have sharp melting points ranging from -40°C to $+180^{\circ}\text{C}$, and their volatilities are dependent upon their chlorine content. Volatility decreases with an increase in chlorination. Chlorinated naphthalenes are used as solvents and extenders for plasticizers, rubbers, elastomers, and synthetic resins. They are good solvents for aliphatic, aromatic, and halogenated hydrocarbons, but have limited solubility for ketones, ethers, and acetates. They are insoluble in alcohols and water. Generally, the "Halowaxes" are compatible with rubber, alkyd resins, petroleum waxes, polystyrene resins, phenolic resins, synthetic elastomers, and plasticizers.

Chloronaphthalene 1000 ("Halowax 1000") is a colorless to pale yellow liquid with a high refractive index. It is a mixture of mono- and dichloronaphthalene, containing 26 per cent of chlorine. It is soluble in almost all organic solvents with the exception of ethyl alcohol. It is insoluble in water and is unaffected by dilute acids and alkalis. Chloronaphthalene 1000 is used as a solvent and extender for Amorphous Wax 190/195, alkyd resins, phenolic resins, synthetic rubber such as Gr-S or "Buna-Al," and many plasticizers. Because of its excellent wetting and penetrating properties, it is employed as a solvent for sludge and varnish.

Monochloronaphthalene 1031 ("Halowax 1031") and Dichloronaphthalene 1037 ("Halowax 1037") are similar in many properties and uses to Chloronaphthalene 1000.

Chloronaphthalene 1001 ("Halowax 1001") is a white, crystalline, waxlike solid, containing 50 per cent of combined chlorine. It is soluble in petroleum

naphthas, aromatic and chlorinated hydrocarbon solvents. It is used as a solvent, a mutual solvent and extender for natural and synthetic rubbers, natural and petroleum waxes, alkyd, polystyrene, phenolic and vinyl resins.

Chloronaphthalenes 1013, 1014, 1051, and 1052 are similar in many respects to 1001 (see Table of Properties).

- I. "Hallowax 1031" is a monochloronaphthalene, white to pale straw in color.
- II. "Hallowax 1000" is composed of mono- and dichloronaphthalene. It is white to pale straw in color.
- III. "Hallowax 1037" is a dichloronaphthalene. It is a white crystalline substance.

	I	II	III
Acidity (mg KOH/g)	0.05 max.	0.05 max.	0.05 max.
Chlorine content (approx.)	22%	26%	32%
Distillation range	5% max. 255°C 95% min. 265°C 98% min. 275°C	80% min. 282°C 90% min. 300°C	4% max. 287°C 95% min. 297°C 98% min. 305°C
Fire point	160°C	171°C	240°C
Flash point	121°C	110°C	130°C
Initial boiling points @ 760 mm	250°C	258°C	275°C
Softening point (M. P.) (approx.)	-25°C	-33°C	50°C
Specific gravity @ 25°C	1.20	1.22	
Specific heat, g cal/g/°C		0.37 @ 85°	
Vis., (Saybolt Univ.) Sec. (approx.)	35 @ 25°C	34 @ 25°C	33 @ 60°C
Volatility (200 g with surface 9.5 sq in for 10 days @ room temp., g/sq in/hr @ 105°C)	1.0%	1.5%	0.75%

- I. "Hallowax 1001" is composed of tri- and tetra-chloronaphthalene. It is white to pale yellow in color.
- II. "Hallowax 1013" is composed of tetra- and penta-chloronaphthalenes. It is light straw colored.
- III. "Hallowax 1014" is composed of penta- and hexa-chloronaphthalenes. It is light yellow in color.

	I	II	III
Acidity (mg KOH/g)	0.05 max.	0.05 max.	0.05 max.
Chlorine content (approx.)	50%	56%	62%
Fire point	None to boiling	None to boiling	None to boiling
Flash point	141°C	180°C	180°C
Initial boiling point @760 mm	308°C	328°C	344°C
Softening point (M. P.) (approx.)	93°C	120°C	137°C
Specific gravity @25°C	1.58	1.67	1.78
Specific heat, g cal/g/°C	0.22 @15° 0.65 @100°		0.19 @15° 0.48 @100°
Vis., (Saybolt Univ.) Sec. (approx.)	30@130°C	33@130°C	35@150°C
Volatility (200 g with surface 9.5 sq in for 10 days @room temp., g/sq in/hr @105°C)	0.010	0.005	0.001

- I. "Halowax 1052" is a heptachloronaphthalene. It is light yellow in color.
- II. "Halowax 1051" is an octachloronaphthalene, light yellow in color.

	I	II
Acidity (mg KOH/g)	0.10 max.	0.10 max.
Chlorine content (approx.)	66%	70%
Fire point (Cleveland O. C.)	None to 430°C	None to boiling
Flash point (Cleveland O. C.)	265°C	None to 430°C
Softening point (M. P.) (approx.)	115°C	185°C
Specific gravity @25°C	1.92	2.00

"AROCLORS"

The "Aroclors" are chlorinated biphenyl and polyphenyls, manufactured by the Monsanto Chemical Company (53). These compounds range in appearance from mobile, oily liquids to hard, transparent resins. They are used as solvents, mutual solvents and extenders for synthetic elastomers, resins, rubbers, waxes, and plasticizers. They are of particular value in preparing synthetic adhesives based on the use of polystyrene, vinyl polymers, ethylcellulose and chlorinated rubbers. The "Aroclors" are compatible with most common plastics and are excellent carriers for pigments used in glass decoration and in mimeograph inks.

- I. "Aroclor 1232" is practically a colorless mobile oil.
- II. "Aroclor 1242" is a practically colorless mobile oil.
- III. "Aroclor 1248" is a yellow-tinted mobile oil.

	I	II	III
Acidity (mg KOH/g)	0.015 max.	0.015 max.	0.015 max.
Average coefficient of expansion (cc/cc/°C)	0.00073 (25-100°C)	0.00068 (25-65°C)	0.00070 (25-65°C)
Color (APHA)	60 max.	100 max.	100 max.
Distillation range ASTM D-20 (Mod.) Corr. °C	290-325°	325-360°	340-375°
Evaporation loss ASTM D-6 (Mod.) 163°C 5 hr 100°C 6 hr	1.0-1.5%	3.0-3.6% 0.0-0.4%	3.0-4.0% 0.0-0.3%
Fire point (Cleveland O. C.)	238°C 460°F	None	None
Flash point (Cleveland O. C.)	152-154°C 305-310°F	176-180°C 348-356°F	193-196°C 379-384°F
Pour point ASTM D-97	-35.5°C -32°F	-19°C 2°F	-7°C 19.4°F
Ref. Index (D-line) @ 20°C	1.620-1.622	1.627-1.629	1.630-1.631
Pounds per gallon @ 25°C	10.55	11.50	12.04
Specific gravity @ 25/25°C	1.266	1.380	1.445
Vis., (Saybolt Univ.) Sec. (ASTM-D-88) @ 210°F @ 130°F @ 100°F	31-32 39-41 47-50	34-35 49-56 80-93	36-37 69-78 185-240

TABLE 58

Resistance of Structural Materials to Aroclors¹⁷

Metals	AROCOLOR NUMBER					
	1248		1254		4465	
	25°C	125°C	25°C	125°C	125°C	5460 125°C
Aluminum.....	R	R	R	R	*RR	RR
Copper.....	R	D	R	D	D	D
Magnesium.....	RR	R	R	R	RR	*RR
Nickel.....	RR	R	R	RR	RR	R
Silver.....	R	R	R	R	R	R
Tin.....	R	R	R	R	R	R
Zinc.....	R	R	R	R	R	RR
Mild Steel.....	RR	R	RR	RR	R	RR
Phosphor Bronze.....	R	D	R	R	R	R
Red Brass.....	D	D	R	D	R	De
Stainless Steel (Type 316).....	RR	RR	RR	RR	RR	RR
Yellow Brass.....	R	Re	R	De	Re	Re
Plastics						
Alkyd Resin No. 46594-12.....	*P	P	*P	P	P	P
Alkyd Resin No. 46594-13 A.....	*D	P	*D	P	P	P
Cellulose Acetate (Fibestos).....	D	P	D	P	P	P
Durite Phenol Furfural Resin.....	*D	P	*R	P	D	P

Formvar Highly Plasticized.....	De	T	Pe	T	T	T
Formvar Low Plasticized.....	PS	T	PS	T	T	T
Glyptal 1276.....	R	P	D	P	P	P
Glyptal 7136.....	*D	T	*R	T	T	T
Maleic Resin No. 46594-13B.....	P	P	*P	P	P	P
Maleic Resin No. 46594-13C.....	P	P	*R	P	P	P
Plexiglas (Methyl Methacrylate).....	*D	P	*D	P	P	P
Polystyrene (Lustron B).....	P	T	P	T	T	T
Resinox Mineral Filled Melamine Resin.....	*D	*P	*R	R	*P	*D
Resinox Wood Flour Filled Melamine Resin.....	*D	P	*R	D	R	P
Resinox Mineral Filled Phenol Formaldehyde.....	*D	D	*D	D	R	P
Resinox Wood Flour Filled Phenol Formaldehyde.....	*D	P	*D	*R	D	P
Resinox Rag Filled Phenol Formaldehyde.....	*D	D	*D	*D	*D	P
Urea Formaldehyde Resin (Plaskon Co.).....	*D	P	*D	*P	P	P

Meaning of Abbreviations:

*—Based on weight *gain* calculated as penetration value shown.

RR—Excellent resistance—less than 1.0×10^{-6} cm/day penetration or .00014 in./yr.

R—Good resistance—has penetration between 1.0×10^{-6} and 10×10^{-6} cm/day or between 0.00014 and 0.0014 in./yr.

D—Doubtful resistance, penetration between 10×10^{-6} cm/day and 100×10^{-6} cm/day or between 0.0014 and 0.014 in./yr.

P—Poor resistance—penetration greater than 100×10^{-6} cm/day or 0.014 in./yr.

PS—Poor resistance due to visible local action although weight change indicates greater resistance.

e—Following the letter indicating resistance signifies material may be better than indicated if totally immersed since weight loss is believed to come from oxidation of the part of test strip exposed to air.

T—Material alone will not stand temperature.

TABLE 59

Solubility of Aroclors¹¹ in 100 Milliliters of Various Solvents

Type of Solvent	Aroclor			1242			1248			1254			1270		4465		5460
		25°C	Hot	Hot	25°C	Hot	25°C	Hot	Hot	25°C	Hot	Hot	Cold	Hot	Cold	Hot	25°C
Acid																	
Acetic Acid.....		S	S	S	S	S	S	S	S	S	S	S	SS	S	SS	S	—
Oleic Acid.....		S	S	—	—	—	—	—	—	—	—	—	—	VS	—	VS	—
Benzoic Acid....		10.0 32c	—	—	10.0 32c	—	—	—	—	—	—	—	—	—	—	—	—
Aldehyde																	
40% Formaldehyde.....		I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	—
Furfural.....		VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	SS	SS	SS	VS	VS	—
Amine																	
Aniline.....		S	S	—	—	—	—	—	—	—	—	—	—	VS	VS	VS	—
Pyridine.....		132.5 30c	440 94c	—	114 31c	425 100c	—	—	—	—	—	—	—	VS	VS	VS	—
Chloro—derivatives																	
Amyl chlorides—mixed		S	S	S	S	S	S	S	S	S	S	S	—	—	VS	VS	—
Carbon Tetrachloride.....		S	S	S	S	S	S	S	S	S	S	S	3.7	—	VS	VS	156
Chloroform.....		S	S	S	S	S	S	S	S	S	S	S	3.0	—	VS	VS	—
Dichlorethylene.....		—	—	—	—	—	—	—	—	—	—	—	—	—	VS	VS	—
Ethylene Dichloride.....		S	S	S	S	S	S	S	S	S	S	S	2.9	—	VS	VS	—
Monochlorobenzene.....		S	S	S	S	S	S	S	S	S	S	S	—	—	VS	VS	—
Orthodichlorobenzene.....		—	—	—	—	—	—	—	—	—	—	—	—	—	VS	VS	—
Tetrachlorethane.....		S	S	S	S	S	S	S	S	S	S	S	3.3	—	VS	VS	—
Trichlorethane.....		S	S	S	S	S	S	S	S	S	S	S	—	—	VS	VS	—
Trichlorethylene.....		S	S	S	S	S	S	S	S	S	S	S	—	—	VS	VS	—
Drying Oil																	
Tung Oil.....		S	S	S	S	S	S	S	S	S	S	S	—	—	VS	VS	—
Linseed Oil.....		S	S	S	S	S	S	S	S	S	S	S	—	—	VS	VS	—

I— Insoluble S— Soluble SS— Slightly Soluble VS— Very Soluble
 Figures show grams of Aroclor per 100 milliliters of solvent at 25°C unless otherwise indicated.

- I. "Aroclor 1254" is a light yellow, viscous oil.
- II. "Aroclor 1260" is a light yellow, soft, sticky resin.
- III. "Aroclor 1262" is a light yellow, sticky, clear resin.

	I	II	III
Acidity (mg KOH/g)	0.015 max.	0.015 max.	0.02 max.
Average coefficient of expansion (cc/cc/°C)	0.00066 (25-65°C)	0.00067 (20-100°C)	0.00064 (25-65°C)
Color (APHA)	150 max.	150 max.	150 max.
Distillation range ASTM D-20 (Mod.) Corr. °C	365-390°	385-420°	400-430°
Evaporation loss ASTM D-6 (Mod.)			
163°C 5 hr	1.1-1.3%	0.5-0.8%	0.5-0.6%
100°C 6 hr	0.0-0.2%	0.0-0.1%	0.0-0.1%
Fire point (Cleveland O. C.)	None	None	None
Flash point (Cleveland O. C.)	None	None	None
Pounds per gallon @25°C	12.82	13.50	13.72
Pour point ASTM D-97	10°C 50°F	31°C 88°F	37°C 99°F
Ref. Index (D-line) @20°C	1.639-1.641	1.647-1.649	1.6501-1.6517
Specific gravity @25/25°C	1.538	1.620	1.646
Vis., (Saybolt Univ.) Sec. (ASTM-D-88)			
@210°F	44-48	72-78	90-103
@130°F	260-340	3200-4500	600-850 (160°F or 71°C)
@100°F	1800-2500		

- I. "Aroclor 1268" is a white, opaque resin.
- II. "Aroclor 4465" is a yellow, transparent, brittle resin.
- III. "Aroclor 5442" is a yellow, transparent sticky resin.

	I	II	III
Acidity (mg KOH/g)	0.25 max.	0.05 max.	0.05 max.
Average coefficient of expansion (cc/cc/°C)	0.00067 (20-100°C)	0.00061 (25-65°C)	0.00123 (25-99°C)
Color (NPA)	1.5 max.	2.0 max.	1.5 max.
Distillation range ASTM D-20 (Mod.) Corr. °C	435-450°	230-320° @ 4 mm Hg	215-300° @ 4 mm Hg
Evaporation loss ASTM D-6 (Mod.)			
163°C 5 hr	0.1-0.2%	0.2-0.3%	0.2%
100°C 6 hr	0.0-0.06%	0.0-0.02%	0.01%
Fire point (Cleveland O. C.)	None	None	>350°C >662°F
Flash point (Cleveland O. C.)	None	None	247°C 477°F
Pounds per gallon @ 25°C	15.09	13.91	12.24
Pour point ASTM D-97			46°C 115°F
Ref. Index (D-line) @ 20°C		1.664- 1.667	
Softening point (ASTM E-28)	135-160°C (hold pt.) 275-320°F (hold pt.)	60-66°C 140-151°F	50-61°C 113-122°F
Specific gravity @ 25/25°C	1.810	1.670	1.470
Viscosity @ 210°F (Saybolt Univ.) Sec. (ASTM D-88)		90-150 (266°F or 130°C)	300-400

- I. "Aroclor 5460" is a yellow, transparent resin.
- II. "Aroclor 2565" is a brown-black, opaque resin.
- III. "Aroclor 1221" is a colorless mobile oil.

	I	II	III
Acidity (mg KOH/g)	0.07 max.	1.4 max.	0.015 max.
Average coefficient of expansion (cc/cc/°C)	0.00179 (25-124°C)	0.00066 (25-65°C)	0.00071 (15-40°C)
Color (NPA)	2.0 max.		50 max. (APHA)
Distillation range ASTM D-20 (Mod.) Corr. °C	280-335° @ 5 mm Hg		275-320°
Evaporation loss ASTM D-6 (Mod.) 163°C 5 hr 100°C 6 hr	0.03% 1.5-1.7% (@ 260°-5 hr)	0.2-0.3%	1.0-1.5%
Fire point (Cleveland O. C.)	None	None	176°C 349°F
Flash point (Cleveland O. C.)	None	None	141-150°C 286-302°F
Pounds per gallon @ 25°C	13.91	14.44	9.85
Ref. Index (D-line) @ 20°C	1.660-1.665		1.617-1.618
Softening point (ASTM E-28)	100-105.5°C 212-222°F	66-72°C 149-162°F	
Specific gravity @ 25/25°C	1.670	1.734	1.182
Pour point ASTM D-97			Crystals @ 1°C Crystals @ 34°F
Vis., (Saybolt Univ.) Sec. (ASTM D-88) @ 210°F @ 130°F @ 100°F			30-31 35-37 40-42

"CLORAFINS"

"Clorafins" are chlorinated paraffins made by Hercules Powder Company (54). They are light amber-colored products, containing about 40 to 50 per cent of chemically combined chlorine. They are miscible with aliphatic, aromatic, and halogenated hydrocarbons, ketones, ethers, and nitro-compounds. They are compatible with the alkyd resins, chlorinated materials, most of the phenolic resins, rosin and rosin derivatives, urea and melamine formaldehyde resins, many of the high polymers, and a variety of natural resins. They are solvents and extenders for resins, rubbers, and elastomers used in coatings and molded products.

PHYSICAL PROPERTIES

	"Clorafin 40"	"Clorafin 42S"	"Clorafin 50"
Chlorine content	40-43.5%	40-43.5%	48-52%
Color (Gardner scale)	6 max.	6 max.	6 max.
Fire point	None	None	None
Flash point	None	None	None
Specific gravity @25/25°C	1.16	1.16	1.26
Viscosity @25°C (poises)	26-39	26-39	430-620

"CHLOROWAXES"

"Chlorowaxes" are products made by Diamond Alkali Company (55). They are chlorinated paraffins, available in both liquid and resinous form. They are excellent solvents for many diverse types of synthetic and natural organic materials. An important use is as a mutual solvent for waxes and synthetic resins, for impregnations, coatings, and moldings. Their presence in a formulation imparts greater moisture, flame and chemical resistance. These products are miscible with ketones, petroleum solvents, halogenated aliphatic and aromatic hydrocarbons, esters, fixed oils, and turpentine; they are immiscible with alcohols, glycols, and water.

PHYSICAL PROPERTIES

Liquid "Chlorowax" LV

Bulking value (gallons per pound)	0.108
Chlorine content	40%
Color (Gardner scale 1933)	1
Evaporation rate @100°C	0.00008 g/sq cm/hr
Heat stability	0.250
Refractive index	1.499
Specific gravity @25/25°C	1.13
Viscosity	
@25°C (Brookfield viscometer)	9 poises
@25°C (Gardner Holdt bubble tubes)	S
@210°F	70 Saybolt uni- versal sec.
@100°F	902 Saybolt uni- versal sec.
Viscosity index	48.5
Weight per gallon	9.4 lb

PHYSICAL PROPERTIES

Liquid "Chlorowax" 40

Bulking value	0.104 gal/lb
Chlorine content	40%
Evaporation rate @100°C	0.00006 g/sq cm/hr
Heat stability	0.450
Pour point	0°C
Refractive index	1.504
Specific gravity @25/25°C	1.15
Viscosity (Brookfield viscometer)	
@25°C	32 poises
@25°C	Z-Z ₁ Gardner Holdt (bubble tubes)
@210°F	166 Saybolt uni- versal sec.
@100°F	3200 Saybolt uni- versal sec.
Viscosity index	82.5
Weight per gallon	9.6 lb
Color (Gardner scale 1933)	2

PHYSICAL PROPERTIES

Liquid "Chlorowax" 50

Bulking value	0.102 gal/lb
Chlorine content	50%
Color (Gardner scale 1933)	2
Evaporation rate @100°C	0.00004 g/sq cm/hr
Heat stability	0.450
Pour point	10°C
Refractive index	1.518
Specific gravity @25/25°C	1.18
Viscosity (Brookfield viscometer)	
@ 25°C	141
@ 25°C	Z ₅ -Z ₆ Gardner Holdt (bubble tubes)
@ 210°F	273 Saybolt uni- versal sec.
@ 100°F	16,970 Saybolt uni- versal sec.
Viscosity index	13.5
Weight per gallon	9.8 lb

PHYSICAL PROPERTIES

Resinous "Chlorowax" 70

Bulking value	0.073 gal/lb
Color, powder	Cream
Density (actual)	13.75 lb/gal
Density (apparent)	7.45 lb/gal
Melting point (ball and ring)	100°C
Particle size	90% through 50 mesh
Odor	None
Refractive index @25°C	1.535
Solubility in water	Insoluble
Specific gravity, solid	1.65
Dielectric constant	
-10 ³ cycles	2.89
-10 ⁶ cycles	2.70
Dielectric strength, 60 cycles	374 volts/mil

Power factor

-10³ cycles

0.530%

-10⁶ cycles

0.065%

Volume resistivity

 3.2×10^{14} ohms/cm

Resinous "Chlorowax 70-S" is a special mixture of "Chlorowax 70" with a small amount of heat stabilizer added when high temperature processing is required. "Chlorowax 70-S" withstands temperatures in the range of 425°F up to one-half hour without decomposing to any appreciable extent. This product is useful as a resin extender and as a flame-retarding agent when processing polystyrene, cellulose acetate-butyrate, and other materials requiring a temperature in excess of 325°F. Its physical properties are essentially the same as those of "Chlorowax 70," in addition to its superior heat stability.

Section IV

BROMINATED HYDROCARBONS

BROMINE

Bromine, the third member of the halogen family, was discovered by the French chemist, A. J. Balard, in 1826. He extracted it from salt after evaporating Mediterranean sea water and named it "muride" from muria meaning brine. The name was later changed to bromine by Gay-Lussac from the Greek bromos meaning "stench," a graphic description of its sharp and disagreeable odor. The unique element had been obtained in Germany a few years prior to Balard's discovery, and a sample was sent to the chemist Liebig. Thinking it was a compound of iodine and chlorine, he set it aside for future study. When he learned the true nature of his sample, he realized the loss of his opportunity, and placed it in a special cupboard labeled "Cupboard of Mistakes."

Bromine is the 25th element in the order of abundance in nature, but it does not occur free because of its great chemical activity. Small quantities occur in many silver ores, but it is more widely distributed, although in sparing amounts, as the bromides of sodium, potassium, magnesium, and calcium in various mineral waters, springs, sea waters, and saline deposits in which the bromine content varies from 0.02 to 0.5 per cent.

The commercial production of bromine was first begun in the United States on a very small scale by Dr. David Alter who, in 1849, operated the salt works at Freeport, Pa. With the industrial production of bromine from the carnallite deposits in Stassfurt, Germany, further efforts were made to develop the bromine industry in the United States. Salt manufacturers of West Virginia and Ohio undertook the recovery of bromine. Although production is small, these continue as active production areas. In 1885, the Midland district of Michigan became a manufacturing center for bromine and its products, manu-

facturing about 40,000 pounds; by 1904, Michigan was far ahead of any state in the size of her output. Despite these sources, the bulk of our supply prior to World War I, was imported from Germany. The Allied Blockade cut off this source causing a serious crisis in which the increased demand for bromine and bromides had to be met by domestic production. In the following years, it became evident that existing means of obtaining bromine failed to meet the expanded needs, especially after the discovery of ethylene bromide as a necessary ingredient of anti-knock gasoline.

In 1924, the United States produced about 2 million pounds of bromine and its compounds; by 1931, the quantity rose to about 9 million pounds, and still larger amounts were demanded. Since the operative sources of bromine could not meet these demands, the only other source appeared to be the ocean. The concentration of bromine, 300,000 tons of bromide per cubic mile of water, or 67 mg per liter (0.0065 per cent), was very small, but with the possibility of efficient methods of extraction, the project would become feasible. The Dow Chemical Company engaged in extensive research which resulted in the development of an electrolytic method, by which bromine could be produced efficiently from the sea. A plant was set up at the mouth of Cape Fear River in North Carolina, and by 1931, 500 pounds of bromine were being extracted daily. In 1933, the Ethyl-Dow Chemical Company increased their plant capacity to produce 15,000 pounds per day. With the advent of World War II, and its increased demands for ethylene dibromide by the automotive and aviation industries, a plant was set up at Freeport, Texas. In 1950, the United States consumed 58,502,000 pounds of bromine and bromine compounds.

All the commercial methods of obtaining bromine are based on its liberation from bromine compounds by the action of chlorine. Generally, the steps involved in extraction include oxidation of the bro-

mide by chlorine, removal of the bromine vapor from solution, condensing or fixing the vapor as a salt or acid, and finally purifying the product.

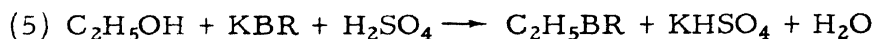
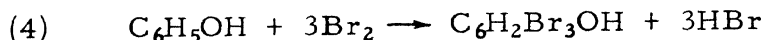
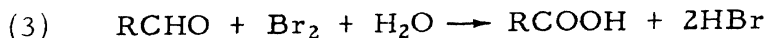
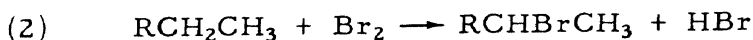
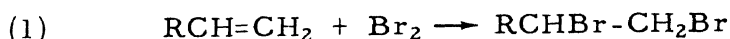
In the process used for extracting bromine from sea water, the first step requires the addition of sulfuric acid to establish the proper hydrogen-ion concentration. After acidifying, it is oxidized with chlorine, the free bromine is blown out of solution by air, sulfur dioxide is added, and this mixture is mixed with water to form hydrobromic acid and sulfuric acid. After further chlorination, bromine is liberated, driven off with steam, collected in liquid form in lead-capped glass bottles, and packed in inert absorbent material in monel drums. It is then shipped in lead-lined tank cars.

Bromine, a reddish-brown liquid, is the only nonmetallic element liquid at ordinary temperature and pressure. With its boiling point at 58.78°C , it vaporizes easily into a reddish-brown gas, having a high density and fairly high atomic weight, 79.916. Bromine gas, being heavy, tends to settle to the floor and flow into any depression. The chemical properties of bromine are intermediate between chlorine and iodine and its reactions are very similar to chlorine, although it is less active than its sister halogen. It is very soluble in all organic solvents and will react with many of them. Its solubility in water at 25°C is 3.35 per cent, but it becomes more soluble in the presence of bromide ions due to the formation of the complexes Br_3^- and Br_5^- . Aqueous solutions of bromine are strong bleaching and oxidizing agents. The strong oxidizing action of bromine causes violent reaction with certain elements such as phosphorus, aluminum, and potassium, giving off light in the process. Bromine unites readily with hydrogen when heated, or when light or catalysts are used.

Organic bromine compounds have long occupied the attention of chemists, and in the past 120 years thousands of organic bromine compounds have been synthesized and studied. Bromine can be introduced

readily into most organic molecules and is more easily replaced by other groups than is possible with chlorine. When a bromo compound is compared with a corresponding chloro compound, they are found to resemble each other, although the bromine compounds are often more dense, less volatile, less combustible, and less stable. It compares more favorably than chlorine in bromination and debromination reactions which frequently can be carried out with lower losses caused by undesirable side reactions.

The reaction of bromine with organic compounds proceeds by one of three methods, depending largely upon the nature of the solvent used and the conditions of the reaction, such as temperature, light, and catalyst. Bromine combines with unsaturated hydrocarbons by the process of addition as, for example, in the preparation of ethylene dibromide. With compounds having replaceable atoms or groups, the products are formed by the process of substitution as with aliphatic hydrocarbons or benzene, under conditions of higher temperature or the presence of a catalyst or both. The third type of reaction is one of oxidation by which such substances as aldehydes are formed.



The earliest bromination of benzene was carried out by Mitscherlich. He obtained benzene hexabromide by the interaction of bromine and benzene using sunlight as a catalyst. Some interesting studies have been made by photobromination, the purpose of which was to determine the mechanism involved when bromine enters the aromatic molecule. These have been summarized in the following data:

SUMMARY OF EXPERIMENTAL DATA (46)

Compounds	Experimental Conditions	Products
Xylenes	Sunlight, high temperature	Xylyl bromide
	Sunlight	Mono- and dibromoxylyl bromides
	Rates in sunlight for m-xylene	Xylyl bromide
	Rates for o, m, p-xylene	Xylyl bromide
	Mn as a carrier	Xylyl bromide
	Mercury lamp, solvent effects	Xylyl bromide
	Mazda lamp, relative rates	Xylyl bromide
Mesitylene	Sunlight	Mesityl bromide
		p-Br-Mesityl bromide
	Sunlight, 140°	Mesityl bromide
1, 2, 4-Trimethylbenzene	Sunlight, one and two atoms Br	Side-chain

Compounds	Experimental Conditions	Products
Tetramethylbenzene	Sunlight, 140°	2, 3, 4-Trimethylbenzyl bromide
Hexamethylbenzene	Mazda lamp, relative rates	Side-chain
Ethylbenzene	Sunlight, 1 and 2 moles Br ₂	1-Br-1-phenylbenzene; 1, 2-dibromobenzene
	Sunlight, relative rates	Side-chain
	Relative rates	Side-chain
	Sunlight, nitrosulfonic acid	Side-chain
Propylbenzene	Sunlight, 1 and 2 moles Br ₂	1-Br-and 1, 2-dibromo-1-phenylbenzene
	Relative rates	Side-chain
Cumene	Sunlight, AlBr ₃	1-Br, 4-Br, and 1,2'-dibromocumene
Butylbenzene	Sunlight, 1 and 2 atoms Br ₂	Alpha-mono-and dibromo products

p-tert-Butyltoluene	Sunlight	Side-chain
o-tert-Butyltoluene	Sunlight	No side-chain
Cymene	Relative rates	Side-chain
Diphenylmethane	Heats of brom. Oxygen effects	Side-chain
Triphenylmethane	Heats of brom. Oxygen effects	Side-chain
Diphenyl	Hg arc, active Br ₂ addition compds.	Addition compds.
as-Diphenylethane	Photobromination	Stilbene and tetraphenylbutadiene
Triphenylethylene	Quantum yields	Addition compds.
Naphthalene	Hg lamp, temp. coef., wave length	Naphthyl bromide
	Hg arc, spectrophotometer	Addition compds.

Compounds	Experimental Conditions	Products
1-Methylnaphthalene	Sunlight, CS ₂	Naphthyl bromide
	Sunlight, 230°	Naphthyl bromide
	Sunlight, boiling hydro-carbon	Naphthyl bromide
	Wave lengths 4050-5790A	Naphthyl bromide
	Hg arc, 230°	Naphthyl bromide
2-Methylnaphthalene	Sunlight, CS ₂	Naphthyl bromide
	Sunlight, 230°	Naphthyl bromide
	Sunlight, high temperature	Naphthyl bromide
	Wave lengths 4050-5790A	Naphthyl bromide
	Philips lamp, Hg arc, effect of glassware	Naphthyl bromide
	Spectrophotometer, iodine effects	{ Naphthyl bromide 1-Br-2-MeNaph.
	Hg arc, 240-60°	Naphthyl bromide

2-Ethyl-naphthalene	Wave lengths 4050-5790A	Side-chain
1, 6-and 2, 6-DiMeNaph,	Wave lengths 4050-5790A	Side-chain
Anthracene	Positive bromine ions	Bromine ions
	Hg arc, active bromine addition	Addition compds.
Phenanthrene	Diffused light, boiling CHCl_3	3, 6-or 3, 9 Dibromophenanthrene
	Intermittent light	9-Br-phenanthrene
	Effect of tert-butyl groups	9, 10 addition
	Effect of different samples	9-Br-phenanthrene
	Excess Br_2 , oxygen, etc.	9-Br-phenanthrene
	Hg arc, active Br compd.	Addition compd.
2-and 3-Tertbutylphenanthrene	Photobromination	9, 10 addition
Fluorene	Boiling CHCl_3 , not direct sunlight	2, 7-Dibromofluorene
	Boiling CCl_4 , Hg arc	9-Bromofluorene
	Sunlight, CCl_4	9-Bromofluorene
	Hg arc, 2 moles Br_2	9, 9-Dibromofluorene

Compounds	Experimental Conditions	Products
Fluorene	Iodine effects, wave lengths	p-Bromofluorene
Stilbene	Rates and effect of heavy radicals	Addition
	Photobromination	Addition
	Temp. coef., wave length	Addition
	Polarized light, temp. coef.	Addition
	Wave lengths, CS ₂	Addition
	Induction periods	Addition
	Induction periods after effects	Addition
	Quantum yields, temp. coef.	Addition
	Inhibitory effects of oxygen	Addition
	Sunlight, relative rates	C ₆ H ₆ Br ₆
Cyclohexane	Vapor phase bromination	C ₆ H ₆ Br ₆
	Temp. coef., wave length	C ₆ H ₆ Br ₆
	Temp. coef., oxygen effects	C ₆ H ₆ Br ₆
	Peroxides	C ₆ H ₆ Br ₆

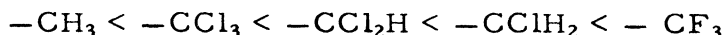
Methylcyclohexane	Peroxides		
1, 4-Dihydronaphthalene	Spectrophotometer	Addition compds.	
Tetralin	Temp. coef., carriers	ac-Dibromo- tetralin	
	Effect of unsat. compds., Hg arc, wave length	Addition compds.	
9, 10-Dihydroanthracene	CS ₂ , CCl ₄ , temp. effects, Hg arc	Dibromide	
o, p-Bromotoluene	Sunlight, excess I ₂ , only nuclear sub.	2, 4-and 2, 5-and 2, 4-or 3, 4-Dibro- motoluene	
p-Bromotoluene	Sunlight, room temp., side-chain sub.	4-Bromobenzyl- bromide	
	Sunlight, side-chain sub.	4-Bromobenzyl bromide	
Chloro- and Bromo- toluene	Hg lamp, relative rates	Chloro-, Bromo- benzyl bromide	

Compounds	Experimental Conditions	Products
o-, p-Bromotoluene	Hg lamp, side-chain sub.	o-p-Bromobenzyl bromide
2, 4-, 2, 6-, 3, 5-Dibromotoluene	Ultraviolet light, side-chain	Benzyl bromides
m-Iodotoluene	Hg lamp, 150-55°, side-chain	m-Iodobenzyl bromide
m-Chlorotoluene	500-watt lamp, 60-90°, CCl ₄	m-Chlorobenzyl bromide
4-Cl, 4-Bromocumene	Diffused light, I ₂ , agitation	4-Cl and 4-Bromol-bromocumene
4-Cl-Ethylbenzene	Sunlight, room temp. silica fl.	4-Cl-1-Bromoethyl benzene
Cl, Br, I-Toluene	300-watt lamps, (irradiation changes, anhydr.)	Benzyl bromides
p-Bromotoluene	300-watt lamps, S effects	p-Bromobenzyl bromide

Of the many uses for bromine and bromine products, the greatest demand is for ethylene dibromide. The discovery of the anti-knock properties of tetraethyl lead in motor fuels in 1922, and the prevention of engine fouling by the addition of ethylene dibromide, saw the beginning of an unprecedented expansion in the bromine industry. Other applications for bromine and its compounds are in the manufacture of bromo-indigo dyes, compounds such as bromoform and acetylene tetrabromide for guage liquids, methylene chlorobromide as a fire extinguisher, and fumigants for pest-infested soil and insect control in food industries. They are also used in photography, in medicinals, and in organic synthesis.

Bromine must be handled with extreme care, because of its highly corrosive nature. It burns the skin quickly, and inhalation of its fumes in large amount is fatal. A slight amount of inhaled gas causes a burning, heavy sensation in the throat and chest.

A study of halogen substitution on the α -carbon atom of N-bromoacetamides revealed a gradual increase in the nuclear bromination of toluene at room temperature, in the following order:



The allylic bromination of cyclohexane decreased in the following order:



At 80°, toluene is found to be 60 times more reactive to bromine than is cyclohexane (42).

TABLE 60
The Competitive Halogenation of Cyclohexane and Toluene¹ (39)

Temp., °C	80	80	80	80	80	80	55	0-2
Reactants								
Cyclohexane	1.486	1.925	0.855	0.789	0.604	0.340	0.325	0.237
Toluene	0.536	1.940	2.610	2.423	1.845	1.068	1.115	1.145
Sulfuryl chloride ²		0.52	0.29					
Chlorine				0.29	0.18	0.12	0.10	0.10
Bromine	0.19							
Products								
Hydrogen chloride						0.113	0.096	0.086
Alkyl halides	0.190	0.497	0.286	0.285	0.174	.114	.105	.112
Benzyl halide	.179	.040	.060	.068	.043	.027	.022	.0318
Halocyclohexane ³	.011	.457	.226	.217	.131	.087	.083	
Cyclohexane ⁴	1.383	1.361	.625	.570	.443	.239	.232	
Toluene ⁴	0.320	1.857	2.548	2.354	1.790	1.038	1.090	
Mole % halogenation	9.4	13.9	8.3	8.9	7.1	8.6	6.9	7.3
Mean cyclohexane-toluene ratio	3.55	0.863	0.287	0.280	0.288	0.275	0.251	
Reactivity of cyclohexane ⁵	0.017	13.2	13.1	11.4	10.6	11.7	15.0	

¹All quantities in moles.

²1% by weight of benzoyl peroxide added

³By difference

⁴Initial quantity minus amount substituted and amount vaporized.

⁵Reactivity of toluene assumed to be 1.00.

PHYSICAL PROPERTIES

Boiling point @ 760 mm Hg	138°F (59°C)
Bromine	99.7% min.
Chlorine	0.1% max.
Color (liquid and vapor)	Dark red
Freezing point	19°F (-7°C)
Molecular weight	159.832
Physical state @ room temperature	Fuming, volatile liquid
Odor	Sharp, harsh, penetrating
Solubility per 100 grams water	3.5 g (approx.)
Specific gravity @ 20/15°C	3.120
Vapor density @ 59°F (15°C)	15.515
Vapor pressure @ 70°F (21°C)	175 mm Hg
Viscosity @ 70°F (21°C)	Approx. that of water

METHYL BROMIDE

Monobromomethane

 CH_3Br

Methyl bromide is a nonflammable gas, with a sweet odor. It is miscible with alcohols, ethers, ketones, esters, and halogenated hydrocarbons, but is only slightly soluble in water, to the extent of 0.097 per cent by weight. It is used as a low-boiling solvent, as a refrigerant, and in organic synthesis.

PHYSICAL PROPERTIES

Boiling point @ 760 mm	4.6°C
Critical temperature	173.3°C
Dielectric constant @ 100°C	0.0068
Flash point (Cleveland O. C.)	None
Freezing point	-93°C
Heat capacity	1.27 (16°C) (0.3-0.6 atm.)
Heat of combustion	184 kg cal/mol
Melting point	-84°C
Molecular weight	94.95

Purity	99.8%
Specific gravity @0/0°C	1.732
Thermal conductivity @0°C	0.574
Vapor pressure	
@ -30°C	130 mm
@ -10°C	380 mm
@ 4.6°C	760 mm
@ 10°C	890 mm
@ 20°C	1250 mm
@ 30°C	1800 mm
@ 40°C	2300 mm
Weight per gallon @0°C	14.4 lb

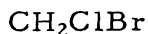
METHYL BROMIDE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
0.55	Methanol	3.55
42.7	Butane	-4.4

METHYLENE CHLOROBROMIDE

Bromochloromethane

Chlorobromomethane



"Chlorbrom"

Methylene chlorobromide is a heavy, clear, colorless liquid, volatile and nonflammable, with a sweet chloroform-like odor. It is miscible in all proportions with alcohol, acetone, benzene, carbon tetrachloride, chloroform, and ether and with most nonaqueous solvents; it is only slightly soluble in Germany during World War II for use as a fire extinguishing fluid. It is now used for the same purpose in the United States, and since it is twice as efficient as carbon tetrachloride, it is used in the midget-type extinguisher. It is corrosive to aluminum and magnesium containers, but it is found to be less corrosive than carbon tetrachloride. It is used as a solvent; as a fire extinguisher for the control of

TABLE 61
Relative Percent Effectiveness of Various Agents,
On Weight Basis, Compared to Methyl Bromide (Methyl Bromide = 100%)
(Comparison of German and Purdue Tests)

Extinguishing Agent	German Air Force Tests		Purdue Tests	
	Agent Concentration (percent vol.) to Extinguish Gasoline Fire in Wind Tunnel	Effectiveness Ratio	Agent Concentration (percent by vol.) to Prevent Ignition of n-Heptane and Air	Effectiveness Ratio
Methyl bromide	15	100	9.7	100
Chlorobromomethane	15	100	7.6	127
Dachlaurin	12-15	100-125	..	...
Carbon tetrachloride	30	50	11.5	84
Dichlorodifluoromethane ("Freon 12")	35	43	14.9	65
Carbon dioxide	45	33	29.5	33

aircraft, electric, and ether types of fires; as a fumigant; as a high gravity liquid for flotation, and as a penetrant for paint removers.

PHYSICAL PROPERTIES

Acidity as hydrobromic acid	0.015% max.
Boiling point @760 mm Hg	67°C
Boiling range @760 mm Hg 5-95% fraction	2° max.
Bromine content	61.76%
Chlorine content	27.40%
Dielectric constant	7.789
Distillation range @760 mm Hg	2° max.
Fire point (Cleveland O. C.)	None
Flash point (Cleveland O. C.)	None
Freezing point	Below -55°C
Melting point	-88°C
Moisture content	0.015% max.
Molal heat of vaporization @25°C	7850 cal
@68°C	7173 cal
Molecular weight	129.399
Pounds per gallon @25°C	16.1
Refractive index N_{25}^D	1.4808
Solubility per 100 grams water @25°C	2.4 g
Specific gravity @25/4°C	1.923
Surface tension @20°C	33.32 dynes/cm
Vapor pressure @25°C	147 millimeters
Viscosity @20°C	0.3486 centistoke

BROMOFORM

Tribromomethane

Formyl tribromide

Methylene tribromide

Methenyl tribromide



Bromoform is a colorless liquid with a sweet, chloroform-like odor. It is miscible with alcohols, ethers, esters, and carbon tetrachloride, but only slightly soluble in water. It forms a constant boiling mixture with butyric acid. It is used as a solvent; in industrial processes where there is need for a high gravity liquid; as an intermediate in organic synthesis; in geological assay, and as a local anesthetic, nervine, and sedative.

PHYSICAL PROPERTIES

Boiling point	148.1 °C
Boiling range, 5-95%	Not more than 5.0 °C
Density @25 °C	2.884
Dielectric constant @20 °C	4.5
Fire point	None
Flash point	None
Freezing point	4.8 °C
Molecular weight	252.8
Specific gravity @25/25 °C	2.847
Surface tension @20 °C	41.53 dynes/cm
Weight per gallon @25 °C	23.69 lb

BROMOFORM FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
2	Acetamide	149.0
72	Acetic acid	118.3
10	Butyric acid	147.6
5	Camphene	148.5
5	Cyclohexanol	149.5
48	Cyclohexanone	158.5
48	Formic acid	97.4
6.5	Glycol	146.8
16	Hexyl alcohol	147.7
12	Isoamyl acetate	150.2

55	Isoamyl alcohol	129.9
65	Isobutyl butyrate	157.7
25	Isobutyl isobutyrate	151.0
19	Isobutyric acid	145.5
	Methyl lactate	152.0
25	α -Pinene	146.5
37	Propionic acid	137.6
10	Propyl sulfide	151.0

ETHYL BROMIDE

Bromoethane

C_2H_5Br

Ethyl bromide is a colorless, low-boiling, volatile liquid with a pleasant ethereal odor. Since it ignites with difficulty, ethyl bromide may be considered as nonflammable. It is completely miscible with ethyl alcohol, ethyl ether, chloroform, carbon tetrachloride, and most common solvents, and only slightly soluble in water. It is used as a volatile solvent, refrigerant, and as a local surface anesthetic. It is also used in the manufacture of phenobarbital and other pharmaceuticals, dyes, and perfumes, and as an ethylating agent in organic synthesis.

PHYSICAL PROPERTIES

Boiling point	38.4°C
Critical temperature	231°C
Dielectric constant, liquid	9.45 (20°C)
Flash point	None
Freezing point	-119°C
Heat of combustion (gas)	340 kg cal/mol
Heat of evaporation	60 cal/g
Purity	Over 98%
Solubility in water @ 0°C	1.055%
@ 10°C	0.956%
@ 20°C	0.906%
@ 30°C	0.888%

Specific gravity @ 25/25°C	1.424
Specific heat @ 5°C	0.22 cal/g
Surface tension @ 10°C	25.48 dynes/cm
@ 20°C	24.5 dynes/cm
@ 40°C	21.52 dynes/cm
Vapor pressure @ -20°C	59 mm
@ -10°C	101 mm
@ 0°C	165 mm
@ 10°C	257 mm
@ 20°C	386 mm
@ 30°C	564 mm
@ 40°C	802 mm
@ 50°C	1113 mm
@ 60°C	1512 mm
Weight per gallon @ 25°C	11.85 lb

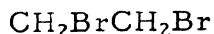
ETHYL BROMIDE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
3	Ethanol	37.6
65	Isoprene	32.0
1	Isopropanol	38.4
32	Isopropyl nitrite	37.7
70	2-Methylbutane	23.5
40	2-Methyl-2-Butene	35.2
50	n-Pentane	33.0

ETHYLENE DIBROMIDE

1,2-Dibromoethane

Ethylene bromide



Ethylene dibromide is a heavy, colorless, non-flammable, stable liquid with a sweet odor. It is insoluble in water but soluble in ethyl ether, ethyl alcohol, carbon tetrachloride, and in most solvents and thinners; it will dissolve oils, fats, gums, waxes, resins, celluloid, etc. It is principally used as a

solvent in tetraethyl lead anti-knock solutions. Since it exerts a powerful dissolvent action upon gums, it is used as a constituent part of lubricating gasolines. It is used in the synthesis of drugs and dyes. It is also used in medicine as an anesthetic, antispasmodic and sedative.

PHYSICAL PROPERTIES

Acidity (0.01 N NaOH/100 cc)	Less than 1 cc
Boiling point	131.4°C
Boiling range	90% within 2.0°C
Density @ 10°C	2.2014
@ 20°C	2.1805
@ 30°C	2.1594
@ 40°C	2.1384
@ 60°C	2.0952
@ 80°C	2.0538
@ 100°C	2.0113
Dielectric constant, 1000 cycle	5.17
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	9.3°C
Latent heat of fusion @ 9.55°C	56.62 joules/g
Latent heat of vaporization @ 130.8°C	193.5 joules
Refractive index @ 25°C	1.5357
Specific gravity @ 25/25°C	2.172
Specific heat	0.18 cal/g/°C
Specific resistivity	2.4 x 10 ⁹ ohms/cm
Surface tension @ 20°C	38.71 dynes/cm
Vapor pressure @ -10°C	2.5 mm
@ 0°C	3.9 mm
@ 10°C	6.03 mm
@ 30°C	17.4 mm
@ 50°C	44.3 mm
@ 70°C	101.0 mm
@ 100°C	295 mm
@ 120°C	552 mm
@ 131°C	760 mm
Weight per gallon @ 25°C	18.07 lb

ETHYLENE DIBROMIDE FORMS AZEOTROPES WITH:

%		B. P. °C of Azeotrope
55	Acetic acid	114.4
44	Butanol	114.8
3.5	Butyric acid	131.1
45	Chlorobenzene	129.8
10	Ethylbenzene	131.1
29	Isoamyl alcohol	125.0
3.5	Glycol	130.9
88	Isoamyl formate	123.7
63	Isobutanol	106.6
6.5	Isobutyric acid	130.5
85	Mesityl oxide	129.2
44	Methyl chloroacetate	127.7
17.5	Propionic acid	127.8
33	Pyrrol	126.3
7	p-Xylene	131.3

ETHYLENE CHLOROBROMIDE

2-Bromo-1-chloroethane

sym-Chlorobromoethane



Ethylene chlorobromide is a colorless, volatile liquid with a chloroform-like odor. It is insoluble in water, but miscible with ethyl alcohol, ethyl ether, carbon tetrachloride, and most organic solvents. It possesses the distinctive property of dissolving both cellulose esters and ethers. It is used as a solvent and in organic synthesis.

PHYSICAL PROPERTIES

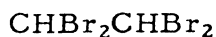
Boiling point	106.1°C
Boiling range	5-95%, not more than 2.0°C
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	-18.4°C
Solubility in water @30°C	0.69 g/100 g solvent
@80°C	0.7 g/100 g solvent
Specific gravity @25/25°C	1.720
Weight per gallon @25°C	14.31 lb

TETRABROMOETHANE

Acetylene tetrabromide

1,1,2,2-Tetrabromoethane

sym-Tetrabromoethane



Muthmann's liquid

Tetrabromoethane is a nonflammable, heavy, white to yellow, oily liquid with a pleasant characteristic odor. It is sparingly soluble in water, but soluble in ethyl alcohol, ethyl ether, chloroform, carbon tetrachloride, and most of the common solvents. It is a good solvent for oils, fats, and waxes. It is used as a solvent; as a fluid in liquid gauges; in microscopy and in separating mineral mixtures.

PHYSICAL PROPERTIES

Boiling point @15 mm	119°C
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	-8.3°C
Melting point	0.1°C
Molecular weight	345.7
Purity	Not less than 98%

Refractive index	1.63795
Solubility in water @ 30°C	0.065 g/100 g solvent
@ 80°C	0.28 g/100 g solvent
Specific gravity @25/25°C	2.953
Weight per gallon @25°C	24.57 lb

PROPYLENE DIBROMIDE

1,2-Dibromopropane



Propylene bromide

Propylene dibromide is a heavy, water-white liquid with a sweet odor. It is only slightly soluble in water, but is soluble in ethyl alcohol, ethyl ether, acetone, benzene and carbon tetrachloride. It is a solvent and is used in organic synthesis.

PHYSICAL PROPERTIES

Boiling range, 5-95%	139.6-142.6°C
Fire point	Nonflammable
Flash point	Nonflammable
Refractive index @25°C	1.519
Solubility in water @ 25°C	0.2% by wt
@ 80°C	0.3% by wt
Specific gravity @25/25°C	1.943
Weight per gallon @25°C	16.2 lb

The brominated aliphatic compounds are used as solvents for gums and waxes. They range from highly volatile compounds to heavy liquids of very little volatility. Some are flammable; many are nonflammable. As solvents, many of these compounds have specialized uses.

The brominated cyclic compounds are effective solvents for a large variety of materials such as dyes, synthetic rubbers, greases, waxes, and tars. They are also used in cleaning and degreasing metals and as special-purpose solvents.

- I. Acetylene tetrabromide, $\text{CHBr}_2\text{CHBr}_2$, is a non-flammable solvent.
- II. Allyl bromide, $\text{CH}_2\text{CHCH}_2\text{Br}_2$, is a special-purpose solvent.
- III. n-Amyl bromide (1-Bromopentane), $\text{CH}_3(\text{CH}_2)_4\text{Br}$.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Odor	Mild, sweet	Sharp	Sweet
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	239°C	70°C	128°C
Boiling range 5-95%	239-242°C	70-71.5°C	128-130°C
Specific gravity @ 25/25°C	2.953	1.415	1.211
Pounds per gallon @ 25°C	24.57	11.8	10.0
Freezing point	0.0°C	<-20°C	<-30°C
Refractive index @ 25°C	1.6326 (20°C)	1.465	1.441
Flash point	None	30°F	90°F
Fire point	None		130°C
Molecular weight	345.7	121.0	151.0
Solubility @ 25°C in Water g/100 g	Infinite in common organic solvents 0.07	Insoluble	Insoluble

- I. Bromodichloromethane, CHBrCl_2 .
 II. Bromotrichloromethane, CBrCl_3 .
 III. n-Butyl bromide, $\text{CH}_3(\text{CH}_2)_3\text{Br}$, is a special-purpose solvent.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Odor	Mild, sweet	Sharp	Sweet
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	89.2°C	103.8°C	101.4°C
Boiling range 5-95%	89.2- 90.6°C	103.8- 105.1°C	101.4- 103.4°C
Specific gravity @ 25/25°C	1.971	1.997	1.274
Pounds per gallon @ 25°C	16.4	16.62	10.60
Freezing point			<-30°C
Refractive index @ 25°C			1.437
Flash point	None	None	75°F
Fire point			130°C
Molecular weight	163.8	198.3	137.0
Solubility @ 25°C in Water g/100 g	Infinite in common organic solvents <1	<0.01	<0.01

- I. sec-Butyl bromide, $\text{C}_2\text{H}_5\text{CHBrCH}_3$.
 II. tert-Butyl bromide, $(\text{CH}_3)_3\text{CBr}$.

Description	I	II
Color	Colorless	Colorless
Odor	Character- istic	Character- istic
Physical state	Liquid	Liquid
Boiling point @760 mm Hg	91.4°C	73.3°C
Boiling range 5-95%	91.4- 91.4°C	73.3- 73.3°C
Specific gravity @25/25°C	1.257	1.215
Pounds per gallon @25°C	10.46	10.11
Freezing point	<-50°C	<-18°C
Refractive index @25°C	1.435	1.425
Flash point	70°F	None
Molecular weight	137.0	137.0
Solubility @25°C in Water g/100 g	Infinite in common organic solvents <0.1 Insoluble	

- I. Cetyl bromide, $\text{CH}_3(\text{CH}_2)_{15}\text{Br}$.
 II. Dibromochloromethane, CHClBr_2 .
 III. Dibromodifluoromethane, CF_2Br_2 .

Description	I	II	III
Color	Dark-yellow	Colorless	Colorless
Physical state	Liquid	Heavy liquid	Heavy liquid
Boiling point @ 760 mm Hg	186°C	118°C	23.2°C
Boiling range 5-95%	186-197°C	118-122°C	
Specific gravity @ 25/25°C	0.991	2.44	2.288 (15/4°C)
Pounds per gallon @ 25°C	8.25	20.3	19.9
Freezing point	15°C	< -20°C	-141°C
Refractive index @ 25°C	1.460		1.3999 (12°C)
Flash point	350°F	None	None
Molecular weight	305.3	208.3	
Solubility @ 25°C in Water g/100 g	Infinite in common organic solvents <0.1	<0.1	<0.1

- I. Isoamyl bromide, $(\text{CH}_3)_2\text{CHC}_2\text{H}_4\text{Br}$.
 II. Isobutyl bromide, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$.
 III. Isopropyl bromide, $\text{CH}_3\text{CHBrCH}_3$.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Odor	Character- istic	Character- istic	Sweet
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	119.7°C	91°C	58.5°C
Boiling range 5-95%	119.7- 121.8°C	91-93°C	58.5- 60.5°C
Specific gravity @ 25/25°C	1.208	1.258	1.304
Pounds per gallon @ 25°C	10.05	10.47	10.85
Freezing point	<-40°C	<-30°C	<-90°C
Refractive index @ 25°C	1.440	1.433	1.422
Flash point	90°F	90°F	None
Fire point	88°F		None
Molecular weight	151.1	137.0	123.0
Solubility @ 25°C	Infinite in common organic solvents		
in Water g/100 g	0.1	Insoluble	Slightly soluble

- I. Lauryl bromide, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{Br}$.
 II. Methylene dibromide, CH_2Br_2 .
 III. Methylene chlorobromide, CH_2BrCl .

Description	I	II	III
Color	Amber	Colorless	Colorless
Physical state	Liquid	Heavy liquid	Liquid
Boiling point @ 760 mm Hg	137°C	95.6°C	67.8°C
Boiling range 5-95%	137- 194°C	95.6- 97.4°C	67.8°C
Specific gravity @ 25/25°C	1.021	2.485	1.930
Pounds per gallon @ 25°C	8.50	20.58	16.06
Freezing point	<-40°C	<-50°C	-88°C
Refractive index @ 25°C	1.457	1.536	1.480
Flash point	295°F	None	None
Fire point		None	None
Molecular weight	249.2	173.9	129.4
Solubility @ 25°C	Infinite in common organic solvents		
in Methanol g/100 g	11	∞	∞
in Water	0.1	Insoluble	2.4

- I. Propylene chlorobromide, $\text{CH}_3\text{CHBrCH}_2\text{Cl}$ and $\text{CH}_3\text{CHClCH}_2\text{Br}$.
- II. Trimethylene bromide, $\text{C}_3\text{H}_6\text{Br}_2$.
- III. Trimethylene chlorobromide, $\text{C}_3\text{H}_6\text{ClBr}$.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Physical state	Liquid	Liquid	Liquid
Boiling point @760 mm Hg	117°C	166.5°C	143°C
Boiling range 5-95%	117- 118.5°C	166.5°C	143- 145°C
Specific gravity @25/25°C	1.540	1.977	1.594
Pounds per gallon @25°C	12.81	16.45	13.27
Freezing point	<-20°C	-33°C	
Refractive index @25°C	1.476	1.520	1.484
Flash point	None	None	None
Fire point			None
Molecular weight	157.5	201.9	157.5
Solubility @25°C in Water g/100 g	Infinite in common organic solvents 0.1	0.2(30°C)	Insoluble

I. Dibromoethylbenzene, $C_6H_3C_2H_5Br_2$.II. Bromobenzene, C_6H_5Br .III. Bromocyclohexane, $C_6H_{11}Br$.

Description	I	II	III
Color	Colorless	Colorless	Slightly yellow
Odor		Character- istic	
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	258°C	156°C	165.8°C
Boiling range 5-95%	258- 266°C	156°C	165.8- 167.3°C
Specific gravity @ 25/25°C	1.744	1.495	1.337
Pounds per gallon @ 25°C	14.51	12.44	11.13
Freezing point	-40°C	-30.6°C	
Refractive index @ 25°C	1.587	1.557	
Flash point	None	51°C	145°F
Fire point	None	155°C	
Molecular weight	264.0	157.0	163.1
Solubility @ 25°C	Infinite in common organic solvents		
in Ether g/100 g	∞	∞	71.3
in Methanol	50	∞	10.4
in VM&P naphtha	∞	71.3	∞
in Water	Insoluble	0.05	0.1
Viscosity @ 25°C centipoises	1.2		2.0

- I. 2-Bromoethylbenzene, $C_6H_5C_2H_4Br$.
 II. o-Bromotoluene, $CH_3C_6H_4Br$.
 III. Bromotoluene mixture, $CH_3C_6H_4Br$.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Odor	Character- istic	Character- istic	Character- istic
Physical state	Liquid	Liquid	Liquid
Boiling point @760 mm Hg		180°C	189.9°C
Boiling range 5-95%		180- 182°C	189.9- 183.2°C
Specific gravity @25/25°C	1.366	1.422	1.419
Pounds per gallon @25°C	11.38	11.83	11.84
Freezing point		-27°C	
Refractive index @25°C	1.558	1.552	1.551
Flash point		175°F	225°F
Fire point		None	
Molecular weight	185.1	171.0	171.0
Solubility @25°C in Water g/100 g	Infinite in common organic solvents 0.1	0.1	0.1
Viscosity @25°C centipoises	1.2	1.3	1.23

- I. Dibromotoluene, $\text{CH}_3\text{C}_6\text{H}_3\text{Br}_2$.
 II. 1-Bromonaphthalene, $\text{C}_{10}\text{H}_7\text{Br}$.
 III. Bromo-m-xylene, $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{Br}$.

Description	I	II	III
Color	Colorless	Faintly yellow	Colorless
Odor	Characteristic		Faint
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	243.7°C		207°C
Boiling range 5-95%	243.7- 245.4°C		207- 209°C
Specific gravity @ 25/25°C	1.836	1.48 - 1.49	1.355
Pounds per gallon @ 25°C	15.26	12.5	11.2
Refractive index @ 25°C		1.65- 1.66	
Flash point	None		
Molecular weight	250.9	207	185.0
Solubility @ 25°C in Water g/100 g	Infinite in common organic solvents Insoluble		Insoluble

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- I. 1,2-Dibromo-3-chloropropane, $\text{CH}_2\text{ClCHBrCH}_2\text{Br}$.
- II. 1,2-Dibromo-1,1-dichloroethane, $\text{CH}_2\text{BrCBrCl}_2$.
- III. Ethylene chlorobromide (1-Bromo-2-chloroethane), $\text{CH}_2\text{ClCH}_2\text{Br}$.

Description	I	II	III
Color	Slightly yellow	Faintly yellow	Colorless
Odor			Chloroform-like
Physical state	Liquid	Liquid	Liquid
Boiling point @760 mm Hg	200°C	176°C	106.1°C
Boiling range 5-95%			106-108°C
Specific gravity @25/25°C		2.26- 2.27	1.720
Pounds per gallon @25°C		18.8	14.31
Freezing point			-18.4°C
Flash point			None
Fire point			None
Molecular weight	236.3	256.8	143.4
Solubility @25°C in Water g/100 g	Infinite in common organic solvents Insoluble	Infinite in common organic solvents Insoluble	Infinite in common organic solvents 0.7

- I. Ethylene dibromide (1, 2-Dibromoethane),
 $\text{CH}_2\text{BrCH}_2\text{Br}$.
- II. Methyl bromide (Bromomethane), CH_3Br , is a
solvent, fumigant, and extinguishing liquid.
- III. n-Propyl bromide (1-Bromopropane),
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Odor	Sweet		Penetrating
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	131.4°C	4.6°C	70°C
Boiling range 5-95%	131-133°C		70-72°C
Specific gravity @ 25/25°C	2.172	1.732	1.333
Pounds per gallon @ 25°C	18.07	14.4	11.1
Freezing point	9.3°C	-93°C	-30°C
Refractive index @ 25°C	1.5357		1.431
Flash point	None	None	None
Fire point	None	None	None
Molecular weight	187.9	94.9	123.0
Solubility @ 25°C	Infinite in common organic solvents		
in Methanol g/100 g	Soluble	∞	∞
in VM&P Naphtha	Soluble	∞	∞
in Water	0.43	0.1	Insoluble

- I. Propylene dibromide (1,2-Dibromopropane), $\text{CH}_3\text{CHBrCH}_2\text{Br}$.
- II. Bromoethylbenzene ("Alkazene 40"), $\text{C}_6\text{H}_4\text{BrC}_2\text{H}_5$.
- III. Bromoisopropylbenzene ("Alkazene 47," Bromocumene), $\text{C}_6\text{H}_4\text{BrC}_3\text{H}_7$.

Description	I	II	III
Color	Colorless	Colorless	Colorless
Odor	Sweet	Characteristic	Characteristic
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	139.6°C	200.5°C	212.4°C
Boiling range 5-95%	139.6- 142.6°C	200.5- 202.8°C	212.4- 216.2°C
Specific gravity @ 25/25°C	1.943	1.339	1.294
Pounds per gallon @ 25°C	16.2	11.2	10.8
Freezing point		-65°C	< -20°C
Refractive index @ 25°C	1.519	1.454	1.536
Flash point	None	93°C	96°C
Fire point	None	135°C	141°C
Molecular weight	201.9	185	199
Solubility @ 25°C	Infinite in common organic solvents		
in Ether g/100 g	Very soluble	∞	∞
in Methanol	Soluble	∞	∞
in Water	0.2	Insoluble	Insoluble
Viscosity @ 25°C centipoises	1.5	1.4	1.6

- I. sec-Amyl bromide, $C_5H_{11}Br$. This is a mixture of sec-amyl bromides used as a solvent for special purposes.
- II. 2-Bromo-4-tert-Butylphenol, $C_6H_3BrC_4H_9OH$, is a special-purpose solvent.
- III. 2-Bromo-p-cymene (Tech.), (2-Bromo-4-isopropyl-1-methylbenzene), $C_6H_3CH_3BrC_3H_7$.

Description	I	II	III
Color	Colorless	Colorless	Straw
Odor	Characteristic	Mild	Pleasant
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	118°C	109°C	120°C
Boiling range 5-95%	118- 120°C	109- 129°C	120- 126.5°C
Specific gravity @ 25/25°C	1.20	1.338	1.253
Pounds per gallon @ 25°C		11.1	10.4
Freezing point		<-20°C	<-20°C
Refractive index @ 25°C		1.550	1.535
Flash point		116°C	104°C
Fire point		160°C	149°C
Molecular weight	151.0	229	213.0
Solubility @ 25°C	Infinite in common organic solvents		
in Methanol g/100 g	∞	∞	50
in Water	Insoluble	Insoluble	Insoluble
Viscosity @ 25°C centipoises		20.8	

- I. 2-Bromoethyl cyclohexane (β -Cyclohexylethyl bromide), $C_8H_{15}Br$.
- II. 2-Bromopentane, $CH_3CH_2CH_2CHBrCH_3$.
- III. o-Bromotoluene, $C_6H_4BrCH_3$.

Description	I	II	III
Color	Colorless	Colorless	Straw
Odor	Mild	Sharp	Characteristic
Physical state	Liquid	Liquid	Liquid
Boiling point @ 760 mm Hg	212.1°C	76°C	180.4°C
Boiling range 5-95%		76-77°C	180.4-181.3°C
Specific gravity @ 25/25°C	1.2334	1.195	1.422
Pounds per gallon @ 25°C	10.3	10	11.9
Freezing point	-56.2°C	<-20°C	<-27°C
Refractive index @ 25°C		1.4387	1.552
Flash point	93.3°C	41°C	79°C
Fire point		52°C	None
Molecular weight	191.0	151.0	171.0
Solubility @ 25°C	Infinite in common organic solvents		
in Water g/100 g	Insoluble	Insoluble	Insoluble
Viscosity @ 25°C centipoises		0.3	1.3

I. 1, 2-Dibromobutane (Butylene bromide),
 $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{Br}$.

II. 1, 2-Dibromocyclohexane, $\text{C}_6\text{H}_{10}\text{Br}_2$.

Description	I	II
Color	Colorless	Colorless
Physical state	Liquid	Liquid
Boiling point @ 760 mm Hg	80-82°C	
Boiling range 5-95%	80-82°C	
Specific gravity @ 25/25°C	1.79	1.79
Pounds per gallon @ 25°C	15	15
Molecular weight	215.9	241.9
Solubility @ 25°C in Water g/100 g	Infinite in common organic solvents Insoluble Insoluble	

Section V

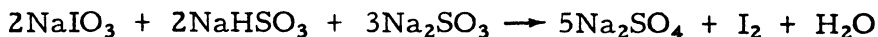
IODINATED HYDROCARBONS

IODINE

Iodine was first discovered in 1811 by Bernard Courtois. While manufacturing saltpeter, he noticed that the sodium carbonate extracted from the kelp corroded the copper vats. After adding sulfuric acid to the mother liquid, violet vapors appeared and condensed to crystalline plates, having a metallic luster. Not having time to investigate this substance, he brought it to the attention of F. Clement and J. B. Desormes, both of whom investigated its properties, but continued to be unaware of iodine as an element. Both J. L. Gay-Lussac and Davy, working independently in 1815, demonstrated conclusively that iodine was an element.

Although iodine is not as active as chlorine and bromine, it is far too active to occur free in nature. It is found in small amounts in sea water as the iodide ion I^- , 1 part of iodide to 8,000 parts of chloride, and as sodium iodate in Chili saltpeter which contains about 0.15 per cent iodine. It is also found in seaweed, in brines of oil wells in which the concentration is only about 0.05 gram of iodine per liter, and in certain animal organs, particularly the thyroid gland. Although the United States consumption of iodine is supplied from kelp, oil well brines, and from the extraction of seaweed, the one to two million pounds consumed is augmented largely from Chili Saltpeter. Some of the brines in California contain 30 to 60 parts per 1,000,000 of sodium iodide.

In the manufacture of iodine from Chile saltpeter, the caliche, or mother liquor, remaining after the sodium nitrate is removed by crystallation, is treated with a mixture of sodium bisulfite and sodium sulfite to reduce the sodium iodate. This mixture must be carefully controlled since an excess will reduce the iodine to the iodide. The iodine in this reaction has a valence number of +5.



Iodine has been of inestimable value in the development of synthetic organic chemistry. Because of its unique properties, it has become a valuable tool in a wide variety of reactions such as Williamson, Wurtz, and Grignard and those of alkyl halides with ammonia and amines. Although the ready reversibility of the reactions between iodine and other substances has seriously limited the development of stable iodine compounds, it has otherwise served as a valuable means of studying the law of mass action and of reaction rates, and of reaction mechanisms.

Iodine, chemically very active, combines with most other elements, except the noble gases, sulfur and selenium. It combines readily with most metals to form iodides but a number of metals in mass form are resistant to iodine because of a protective film produced by the interaction of an initial layer of metal and iodine. Its combination with hydrogen is incomplete since hydrogen iodide is unstable at temperatures high enough to cause a reaction between iodine and hydrogen. However, in the presence of a platinum catalyst, iodine and hydrogen may be combined at moderately high temperatures.

When iodine is liquefied by heat (melting point 113.6°C), it is a good solvent for the alkali metal iodides from ammonium bases. Liquid iodine is the only element exhibiting considerable ionizing power as a polar solvent despite its relatively low dielectric constant, which is about 12.0. Compared to the other halogens, iodine reacts less violently with organic compounds and owing to the weakness of the carbon-iodine bond, the reactions are frequently reversible.

Iodination by substitution can be achieved in which iodo derivatives and hydrogen iodide are formed. But only small yields are possible, since a reverse reaction occurs in which elemental iodine is liberated from the hydrogen iodide and iodo compound, and is replaced by hydrogen. In the presence of an oxidizing agent which converts the hydrogen iodide to free iodine or which neutralizes it by a basic

substance, it becomes possible to complete the substitution reaction. Nitric acid has been used as an oxidizing agent to complete the substitution reaction.

Iodination by addition with unsaturated hydrocarbons from which polyiodo derivatives are formed can be achieved, but more often the saturation is incomplete and with frequent reversibility of reaction. Such reactions will occur with other unsaturated compounds. The organic iodo compounds are less stable than the other organic halogen compounds. Of the alkyl monoiodo compounds, those containing the iodine in a primary attachment to the carbon are the most stable; the secondary compounds are less stable, and tertiary compounds are the least stable.

Iodinated aliphatic compounds are made by one of three methods: (1) by the action of hydriodic acid or phosphorus triiodide on an alcohol, (2) by the addition of iodine to an olefin, and (3) by the replacement of chlorine or bromine in a halogenated derivative with iodine, using an alkali iodide in an appropriate solvent.

Iodinated hydrocarbons differ from the chlorinated or brominated analogs by having lower vapor pressures, higher density, and lower stability.

Many iodonium compounds have been produced directly from the aromatic hydrocarbons or their derivatives which exhibit properties that are of interest for such uses as dyes, detergents, flotation reagents, surface-active agents, etc. An iodine compound, 2-amino-4-nitroiodobenzene, has been prepared which is found to be 1250 times as sweet as sucrose.

Datta and Chatterjee (48) have found that iodine will enter the aromatic ring in the presence of nitric acid, yielding the following compounds:

benzene	→	moniodobenzene
toluene	→	o-and p-iodotoluene
o-xylene	→	4-iodo-o-xylene
m-xylene	→	4-iodo-m-xylene
p-xylene	→	2-iodo-p-xylene
mesitylene	→	moniodomesitylene
ethylbenzene	→	moniodoethylbenzene
cymene	→	moniodocymene
naphthalene	→	moniodonaphthalene

p-Phenol and salicylic acid are almost quantitatively diiodinated when treated with iodine dissolved in ethyl alcohol in the presence of a mineral acid such as sulfuric, nitric, hydrochloric or phosphoric acid (49).

Alkyl iodides have been prepared from the action of iodine, a mixture of red and yellow phosphorus, and the corresponding alcohol (50).

Iodine attached to an aromatic ring is more stable than when it is attached to an aliphatic compound. The order of reactivity of the halogens where the acyl, aryl, and alkyl groups are concerned, is as follows: $I > Br > Cl > F$ (51).

METHYLENE DIIODIDE



Methylene diiodide is a very heavy, highly refractive liquid. Its specific gravity of 3.325 is the highest of any pure liquid, with the exception of mercury. It is miscible with alcohols, aromatic and aliphatic hydrocarbons, ethers and halogenated hydrocarbons. It is an excellent solvent for sulfur and phosphorus, and is used as a special-purpose solvent.

PHYSICAL PROPERTIES

Boiling point	181°C
Density	3.325
Melting point	6.0°C
Molecular weight	267.9
Refractive index	1.7557
Solidifies	5.2°C
Specific gravity	3.325

IODINATED COMPOUNDS

	Description	Density	M. P.	B. P.	Refractive Index	Solubility
n-Butyl iodide $\text{CH}_3\text{CHICH}_3$ Mol. Wt. 184	Colorless to brown	1.617		131°C	1.5001	Alcohol Ether Water (insol)
Isobutyl iodide $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ Mol. Wt. 183	Colorless to brown liquid	1.605	-93°C	120°C	1.4960	Alcohol Ether Water (insol)
sec-Butyl iodide $(\text{CH}_3)_2\text{CHCH}_2\text{I}$ Mol. Wt. 183	Colorless to brown liquid	1.626		119-120°C		Alcohol Ether Water (insol)
Ethyl iodide $\text{CH}_3\text{CH}_2\text{I}$ Mol. Wt. 156	Colorless to brown liquid	1.950	-108°C		1.5168	Alcohol Ether Water (insol)
Methyl iodide CH_3I Mol. Wt. 142	Colorless to brown liquid	2.28	-66.5°C	42.5°C		Alcohol Ether Water (insol)
Propyl iodide (iso) $\text{CH}_3\text{CHICH}_3$ Mol. Wt. 170	Colorless to brown liquid	1.703	-90°C	89-90°C	1.5026	Alcohol Ether Water (insol)
Propyl iodide (n) $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ Mol. Wt. 170	Colorless to yellow liquid	1.747	-98°C	102-103°C	1.5051	Alcohol Ether

1-Chloro-2-iodobenzene			0-2°C			113-114°C @ 14 mm	
1-Chloro-3-iodobenzene						171-2°C	Water (insol)
Dichloroiodoethane $\text{ICH}_2\text{CHCl}_2$	Liquid	2.219				131°C	Water (insol)
Dichloroiodomethane Cl_2CHI	Liquid	2.403					
Dibromoiodomethane ICHBr_2	Solid		22.5°C				
Diiodoacetylene $\text{IC}\equiv\text{CI}$	Liquid		78-82°C			80-100°C	
Diiodobutane-1,4 $\text{I}(\text{CH}_2)_4\text{I}$	Liquid	2.307	5.8°C			120-5°C @ 12 mm	
Diiodopentane-1,5 $\text{I}(\text{CH}_2)_5\text{I}$	Oil	2.194	9°C			149°C @ 20 mm	
Diiodopropane-1,2 $\text{CH}_3\text{CH}_2\text{ICH}_2\text{I}$	Liquid	2.490				d	
Diiodopropane-2,2	Liquid	2.15				147.8d	
Diiodopropane-1,3	Liquid	2.561	-13°C			168-70°C @ 170 mm	
Iodobenzene $\text{C}_6\text{H}_5\text{I}$ Mol. Wt. 204	Liquid	1.824	-28.5°C			188.6°C	Alcohol (sol) Ether Chloroform Water (insol)
Iodoethyl Acetate	Liquid	2.441				184°C	
o-Iodotoluene $\text{IC}_6\text{H}_4\text{CH}_3$	Liquid	1.698				211-2°C	Alcohol Ether Water (insol)

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