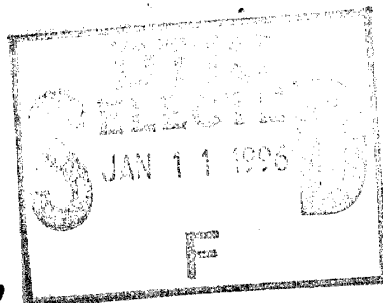
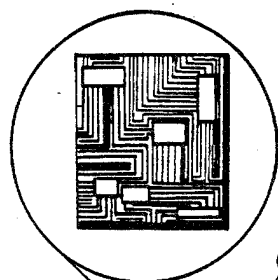


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HALOCARBONS AS HALON REPLACEMENTS: PHASE II LABORATORY TESTING OF HALON 1211 REPLACEMENTS

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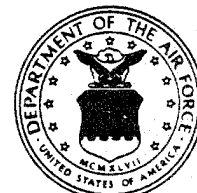
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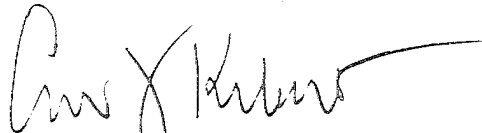
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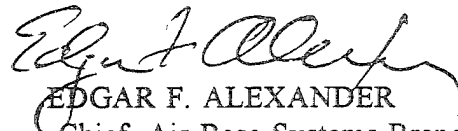
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PREFACE

This report was prepared by the Advanced Protection Technologies (APT) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico 87131, for Wright Laboratories, Air Base Fire Protection and Crash Rescue Systems Branch, Tyndall Air Force Base, Florida 32403-6001 under Subtask 2.03, "Halocarbons as Halon Replacements," Contract F29601-87-C-001. This report covers Phase II of that project as it applies to Halon 1211 streaming replacement agents and summarizes work accomplished between December 1988 and May 1992. The Phase II effort for Halon 1301 total-flood agent replacement is documented in a separate report. The WL/FIVCF Project Officer was Dr. Charles J. Kibert, and the Principal Investigator was Dr. Robert E. Tapscott.

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the overall effort was to develop one or more clean, halocarbon fire-extinguishing agents to replace Halons 1211 and 1301. The goal of the Phase II effort to identify a Halon 1211 replacement includes a description of laboratory results to date, a review of predictive methods for selected properties of halocarbons, and the estimation of selected properties for compounds of interest. A further objective was to select candidate agents for further testing, including medium-scale (4-ft²) field tests.

B. BACKGROUND

Halon firefighting agents have been used for many years. Because of their combination of effectiveness, cleanliness, safety, and relatively low cost, little incentive has existed in the past to develop new chemicals. Since 1966, however, concerns about the environmental impact of halons has been increasing. Calculations and experimental data indicate that halons deplete stratospheric ozone more severely, on a per-pound basis, than do chlorofluorocarbons. The dangers posed by chlorofluorocarbons (CFCs), halons, and other volatile halocarbons to the atmosphere through both stratospheric ozone depletion and greenhouse effects are becoming increasingly evident. As a result of these concerns, the present halon fire-extinguishing agents will be phased out by 1 January 1994 under an international treaty. The United States Air Force has placed a high priority on the development of substitute agents to replace halon fire suppressants.

In Phase I of this project, all information collected during previous work was reviewed and updated, and experimental plans were prepared. The Phase I efforts for Halon 1211 replacement and for Halon 1301 replacements have been documented.^{1,2}

¹ Nimitz, J. S., Tapscott, R. E., Skaggs, S. R., and Moore, T. A., *Halocarbons as Halon Replacements: Technology Review and Initiation*, ESL-TR-90-38, Vol. 1 of 5, Air Force Engineering and Services Laboratory, Tyndall Air Force Base, Florida, July 1990.

C. SCOPE

The scope of this overall task involves the development of one or more halocarbon replacements for Halons 1211 and 1301. The target criteria for the replacement agents are that (1) the agent leaves no residue upon evaporation; (2) the ODP (ozone-depletion potential) be 0.05 or less on either a per-molecule basis or a unit-weight basis when compared with CFC-11; (3) the estimated or reported acute toxicity be equal to or better than that of the halon being replaced; (4) other environmental impacts be equal to or less than that of the halon being replaced; and (5) no major changes in Air Force equipment be required for storage, transfer, or delivery.

This report gives cup-burner extinguishment results for 47 compounds, reviews estimation methods for properties of interest, and presents ranked lists of Halon 1211 candidate replacement agents.

D. METHODOLOGY

The laboratory tests involved the NMERI 5/8-scale cup burner using *n*-heptane fuel. The methods used for property prediction included theoretically-based equations, group additivity, quantum mechanical calculations, molecular connectivity, and fully empirical correlations. New algorithms were developed for estimation of selected properties. The cup-burner data were used to develop an improved algorithm for estimating flame suppression ability of haloalkanes based on chemical structure. New and previously reported algorithms were applied to predict selected properties for all haloalkanes in the NMERI HALOCARBON DATABASE. The APT/CGET LIBRARY DATABASE was used throughout this project to store information on literature references.

² Tapscott, R. E., Skaggs, S. R., Dierdorf, D. S., and Moore, T. A., *Halocarbons a Halon Replacements: Phase I—Technology Review and Initiation, Halon 1301 Replacements*, ESL-TR-90-38, Vol. 2 of 5, Wright Laboratories, Tyndall Air Force Base, Florida, March 1993. (Draft)

E. TEST DESCRIPTION

The NMERI 5/8-scale cup burner was used to obtain flame extinguishment concentrations using standard methodologies employed in past testing of agents as halon replacements.

F. RESULTS

Candidate halocarbons for medium-scale field testing as replacement streaming agents for Halon 1211 have been identified and their properties have been tabulated. Laboratory results show that bromine atoms provide the greatest chemical extinguishment, closely followed by iodine atoms. The larger a molecule (e.g., the greater the number of carbon atoms), the greater is its vapor-phase heat capacity and the better physical extinguishment it provides.

G. CONCLUSIONS

Only two agents show promise as near-term replacements for Halon 1211—perfluorohexane ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$, tetradecafluorohexane, FC-5-1-14) and 2,2-dichloro-1,1,1-trifluoroethane (CHCl_2CF_3 , HCFC-123). These materials have a sufficiently high boiling point to enable their use in streaming. HBFC-22B1 is a highly effective agent; however, it has a high ODP and is likely to be unacceptable over the long term. HFCs appear to be the most promising family of chemicals owing to their zero ODP and relatively low global warming potential (GWP); however, at the time that this work was done, no near-term HFCs with higher boiling points had been identified.

Bromofluoroalkenes and fluoroiodoalkanes show promise as effective, low-ODP, second-generation extinguishants. These materials will have very low or zero ODPs and GWPs and should be highly effective, although testing is needed. Geminal hydrodibromoalkanes are organic compounds containing two bromine atoms on the same carbon atom. Such materials have two modes of tropospheric destruction. The

geminal bromine atoms allow photolysis, and the hydrogen atom reacts with tropospheric hydroxyl free radicals. However, the geminal hydrodibromoalkanes will have higher ODPs than either the alkenes or the iodinated compounds, and the ODPs may be too high for long-term use.

Property estimation is a valuable tool for agent screening. Techniques exist for estimation of physical, chemical, environmental, and toxicological properties of interest with sufficient accuracy for initial screening of candidates. A new algorithm allows improved estimation of fire suppression concentrations.

H. RECOMMENDATIONS

The first-generation candidate agents identified should be tested at medium-scale to determine their performance as streaming agents. In addition, selected second-generation agents should be tested at laboratory scale, and eventually at large scale.

Although near-term, first-generation agents will be the major emphasis in this particular program, work should be started as soon as possible on second-generation agents, particularly those that have been indicated herein as having low-ozone depletion potentials and high effectiveness. To allow expansion of the set of second-generation candidates, additional properties should be estimated, including photolytic cross sections, rates of reaction of bromine- and iodine-containing compounds with $\cdot\text{OH}$, temperature sensitivities, and GWPs. Once these properties have been estimated, candidate agents should be screened further. The most promising should be obtained (synthesized if not commercially available) and tested for effectiveness, toxicity, and environmental effects. Experiments to determine photolytic cross sections and rates of reaction of selected HBFCs with $\cdot\text{OH}$ should be conducted, and the results used to calculate atmospheric lifetimes and ODPs.

TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION	1
	A. OBJECTIVE	1
	B. BACKGROUND	1
	C. SCOPE	2
II	PRIORITIZATION, GROUPING, AND PROPERTY ESTIMATION FOR CANDIDATES	4
	A. GROUPING OF CHEMICAL CANDIDATES	4
	B. PHYSICAL PROPERTY PREDICTION	4
	C. DEVELOPMENT OF ESTIMATION METHODS	7
	D. TOXICOLOGICAL INDICES	8
	E. TRENDS	10
	F. GROUP 1 CANDIDATES	10
III	LABORATORY-SCALE TESTING	13
IV	FIRE EXTINGUISHMENT PREDICTION	16
V	SECOND-GENERATION AGENTS	19
VI	PHYSICAL PROPERTY PREDICTIONS	23
	A. INTRODUCTION	23
	B. GROUP ADDITIVITY	23
	C. CORRESPONDING STATES	25
	D. QUANTUM MECHANICAL CALCULATIONS	25
	E. MOLECULAR CONNECTIVITY	29
	F. EMPIRICAL CORRELATIONS	34
VII	BIOLOGICAL STRUCTURE-ACTIVITY RELATIONSHIPS	36
	A. INTRODUCTION	36
	B. STRATEGY FOR FORMULATING A QSAR	38
	C. SELECTION OF PHYSICOCHEMICAL PARAMETERS	39
	1. Hydrophobicity (Lipophilicity)	39
	2. Polar or Electronic Effects	40
	3. Steric Effects	41
	4. Molecular Structure Descriptors	43

TABLE OF CONTENTS (CONCLUDED)

Section	Title	Page
	D. DATA REQUIREMENTS FOR QSAR DEVELOPMENT	44
VIII	RESULTS, CONCLUSIONS, AND RECOMMENDATIONS	45
	A. RESULTS	45
	B. CONCLUSIONS	45
	C. RECOMMENDATIONS	46
REFERENCES		49
APPENDICES		
	A ESTIMATION METHODS FOR PROPERTIES OF INTEREST	53
	B SELECTED REFERENCES ON PREDICTION OF PHYSICAL PROPERTIES	126
	C TWO SIMPLE SERIES FOR DETERMINATION OF EMPIRICAL CORRELATIONS	134

LIST OF TABLES

Table	Title	Page
1.	SURVEY OF AVAILABILITY OF LITERATURE DATA.	5
2.	PRIORITIZATION OF PROPERTIES FOR FIREFIGHTING	6
3.	SURVEY OF ESTIMATION METHODS FOR HALOALKANE PROPERTIES	9
4.	LIST OF ALL POSSIBLE ONE-CARBON HALOCARBONS.	11
5.	CANDIDATE HALON REPLACEMENTS FOR COMMERCIALIZATION	12
6.	EXTINGUISHING CONCENTRATIONS, 5/8-SCALE CUP BURNER . .	14
7.	SELECTED ALKENE SECOND-GENERATION CANDIDATES	20
8.	FLUOROIODOCARBONS IN ORDER OF INCREASING BOILING POINT	21
9.	PROPERTIES OF FLUOROIODOCARBONS	22
10.	BOND TYPES AND NONIODINATED ONE-CARBON SUBSTITUENTS	24
11.	VALENCE DELTA VALUES FOR SP ³ CARBON AND FLUORINE . .	32
12.	VALENCE DELTA VALUES FOR CHLORINE, BROMINE, AND IODINE	33
13.	ATOMIC CONTRIBUTIONS TO MOLAR REFRACTION	42
14.	TOP CANDIDATE SECOND-GENERATION STREAMING AGENTS .	47
A-1.	C-H BOND POLARITY INDEXES (F VALUES)	56
A-2.	PREDICTED LIFETIMES FOR 1- AND 2-CARBON HFCs, HCFCs . . .	62
A-3.	EXPERIMENTAL PARAMETERS FOR SELECTED HALOCARBONS .	70
A-4.	RANGES OF INTERATOMIC FORCES	73

LIST OF TABLES

Table	Title	Page
A-5.	BOND STRENGTHS FOR COVALENT BONDS TO SP ³ CARBON . . .	73
A-6.	GROUP ADDITIVITIES FOR C-H BOND STRENGTHS	74
A-7.	C-H BOND STRENGTH ESTIMATES FOR TRIHALOMETHANES . . .	75
A-8.	BOND DISSOCIATION ENERGIES FROM HEATS OF FORMATION CALCULATED WITH THE AM1 PARAMETERIZATION.	77
A-9.	HEATS OF FORMATION OF ONE-CARBON FREE RADICALS OF HALOGENATED HYDROCARBONS AT 298K	80
A-10.	CRITICAL CONSTANT INCREMENTS	83
A-11.	CALCULATED DIPOLE MOMENTS FOR 1-CARBON HALOALKANES	86
A-12.	REPORTED LIFETIMES, TEMPERATURE SENSITIVITIES, GWPs	90
A-13.	HEATS OF FORMATION OF COMMON HALOCARBON COMBUSTION PRODUCTS	91
A-14.	CALCULATED AND EXPERIMENTAL HEATS OF FORMATION . . .	94
A-15.	HEATS OF REACTION FOR ALL ONE-CARBON HALOALKANES . .	97
A-16.	TOXICITY CLASSES	100
A-17.	MOLAR VOLUME ADDITIVITY FACTORS	101
A-18.	CONTRIBUTIONS FOR I IN SOUDERS' EQUATION	103
A-19.	ATOMIC CONTRIBUTIONS TO MOLAR REFRACTION	105
A-20.	CANDIDATE COMPOUNDS FOR ODP CALCULATIONS	110
A-21.	MOPAC CALCULATED POLARIZATION VOLUMES	114
A-22.	THEORETICAL HEAT CAPACITY AT CONSTANT PRESSURE . . .	117
A-23.	GROUP CONTRIBUTIONS TO HEAT CAPACITIES, kJ/mol-K	119

LIST OF ABBREVIATIONS AND ACRONYMS

APT	Advanced Protection Technologies
BCF	bioconcentration factor
BDE	bond dissociation energy
CAS	Chemical Abstract Services
CFC	chlorofluorocarbon
CGET	Center for Global Environmental Technologies
EPA	Environmental Protection Agency
GWP	global warming potential
HCFC	hydrochlorofluorocarbon
IRCS	International Research Communications System
LSDE	laboratory-scale discharge extinguishment apparatus
LSER	linear solvation energy relationship
MINDO	Modified Intermediate Neglect of Differential Overlap
MNDO	Modified Neglect of Differential Overlap
NCSS	Number Cruncher Statistical System
NMERI	New Mexico Engineering Research Institute
NTIS	National Technical Information Service
ODP	ozone-depletion potential
PA	Public Affairs
PVT	pressure-volume-temperature
QSAR	quantitative structure-activity relationship
SAR	structure-activity relationship
SCF	self-consistent field
TSCA	Toxic Substances Control Act

LIST OF SYMBOLS

a	absorption coefficient
A	parameter in extinguishment concentration and activation energy algorithms and in Antoine equation
$[A]$	concentration of absorbing species
AD_{50}	anesthetic dose for 50 percent of an animal population
B	parameter in extinguishment concentration and activation energy algorithms and in Antoine equation; boiling point
B_n	thickness of a given molecular substituent along its main axis
C	concentration; parameter in extinguishment concentration and activation energy algorithms and in Antoine equation; heat capacity
C_p	heat capacity at constant pressure
C_v	heat capacity at constant volume
c	speed of light
c_k	coefficient of ψ_k in linear combination of 1-electron wave functions
d	density
$d\tau$	differential element for the coordinates of a quantum mechanical system
D	parameter in extinguishment concentration and activation energy algorithms; bond dissociation energy
E	energy; parameter in extinguishment concentration and activation energy algorithms
E_a	activation energy
$\bar{E}$	approximate energy
EC_{50}	effective concentration for 50 percent of a population
E_s	Taft parameter
e	elementary charge
F	cup-burner fire suppression concentration; Swain and Lupton polarity index

LIST OF SYMBOLS (CONTINUED)

$\hbar$	Planck's constant divided by 2π
h	number of hydrogen atoms suppressed; Planck's constant
ΔG	change in free energy
$\hat{H}$	Hamiltonian quantum mechanical operator
H	Hamiltonian matrix
ΔH	change in enthalpy
I	intensity of light
$J(\lambda)$	actinic irradiance at wavelength λ
k	Boltzmann constant; absorbance
k'	pseudo first-order rate constant
K_{ow}	octanol-water partition coefficient
K_o	rate constant
K_a	logarithm of acid dissociation constant
l	pathlength
L	length of a molecule along its longest axis
LC_{50}	lethal concentration for 50 percent of an animal population
m	mass
M	molecular weight; molar mass
MR	molar refraction
n	refractive index; number density; moles
n_o	Loschmidt number
N	Avogadro's number
N_{Br}	number of bromine atoms in a molecule

LIST OF SYMBOLS (CONTINUED)

N_C	number of carbon atoms in a molecule
N_{CF_3}	number of CF_3 groups in a molecule
N_{Cl}	number of chlorine atoms in a molecule
N_F	number of fluorine atoms in a molecule
N_H	number of hydrogen atoms in a molecule
N_I	number of iodine atoms in a molecule
P	pressure; parachor
P_r	reduced pressure
p_0	normal atmosphere
q	charge; molecular partition function
Q	heat
Q_H	C-H bond polarity
R	gas constant; molar refraction
$\mathcal{R}_\infty$	Rydberg constant
S	overlap matrix
ΔS	change in entropy
T	temperature
T_r	reduced temperature
U	internal energy
V	molar volume
V_0	standard volume
$\hat{V}$	potential energy operator
z	compressibility constant

LIST OF SYMBOLS (CONCLUDED)

Z_v	number of valence electrons
α	polarizability
δ	vertex degree or valence; parameter in Taft parameter definition
∇^2	differential operator $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$
ϵ_0	permittivity of vacuum
λ	wavelength
μ	chemical potential; dipole moment; viscosity
Φ	quantum yield
ρ	liquid density
ψ	quantum mechanical wave function
ψ^*	complex conjugate of ψ
φ	one-electron quantum mechanical wave function
σ	standard deviation; Hammett sigma constant; absorption cross section
τ	tropospheric lifetime
θ	zenith angle
ν	frequency
$\bar{\nu}$	wave number
$^1\chi$	first-order molecular connectivity index
$^2\chi$	second-order molecular connectivity index
ϵ	absorbance

SECTION I

INTRODUCTION

A. OBJECTIVE

The overall objective of this effort is to develop clean halocarbon firefighting agents to replace Halon 1211 for streaming applications and Halon 1301 for total flooding. One objective of Phase II of the Halon 1211 replacement effort was to test candidate Halon 1211 replacements at laboratory-scale in neat form and in blends. Another purpose was to determine flame-extinguishment concentrations for a broad range of haloalkanes to develop an improved predictive algorithm for fire-suppression capabilities. In addition, methods for estimating physical, biological, and environmental properties of halocarbons for which experimental values are unavailable were to be developed. These new methods will facilitate the screening of candidate agents in future work. A final objective was to rank candidate agents for future testing.

B. BACKGROUND

Work performed under the Air Force project "Next-Generation Fire Extinguishing Agent" laid a foundation for the development of new firefighting agents. In Phase I of that project, the theory and technology of fire suppression were reviewed and used to establish directions for continuing agent development (Reference 1). In Phase II, selected laboratory experiments on replacement agents were performed (Reference 2). Phase III initiated work on a training agent replacement (Reference 3), and Phase IV provided additional test data on replacement training agents (Reference 4). The purpose of these two phases was to determine whether the development of replacements for training agents was a viable option and to find the most promising directed approach in such an effort. Phase V of "Next-Generation Fire Extinguishing Agents" supplied the initial versions of needed databases on candidate agents for both training and general firefighting use (Reference 5). These databases included information on ozone depletion, toxicity, physical properties, and

availability. Ozone-depletion potential (ODP) and fire suppression prediction methodologies were also proposed and construction of a literature database was initiated.

Based on the results of the Next-Generation Agent project, two independent efforts were initiated. "Alternative Training Agents" initiated an effort directed toward development of a halon replacement for firefighter training only. "Halocarbons as Halon Replacements" is directed toward development of general-purpose halon replacement agents.

"Alternative Training Agents" had four phases. Phase I included a technology review and developed methodologies for predicting agent properties (Reference 6). Laboratory- and medium-scale experimental studies were carried out in Phases II and III (References 7 and 8). The final agents selected (HCFC-123 and blends) were validated in Phase IV (Reference 9).

"Halocarbons as Halon Replacements" was initially directed only toward a Halon 1211 replacement; however, the project was later amended to include replacement of Halon 1301. As amended, the subtask requires separate reports for the Halon 1211 and Halon 1301 efforts in each of three phases; however, owing to decreases in Air Force resources, Phase III work on Halon 1301 replacements was discontinued at the request of the Air Force. The Phase I effort applicable to Halon 1211 replacement is documented in Reference 10. Reference 11 documents the Phase I effort for a Halon 1301 replacement. The present report covers the Phase II effort on Halon 1211 replacements.

C. SCOPE

This report gives laboratory results on 47 compounds, reviews estimation methods for properties of interest, and gives lists of both first- and second-generation Halon 1211 replacement candidate agents. Estimates are made for selected physical properties and estimated values have been added to better complete the NMERI HALOCARBON DATABASE for which these data are not reported.

This study reviews methods for estimating the properties of haloalkanes that are of potential interest for firefighting and other applications. These properties include anesthetic dose, atmospheric lifetime, bioconcentration factor, bond strengths, boiling point, dielectric constant, dipole moment, fire suppression concentration, global warming potential, heat of formation, heat of reaction in flames, heat of vaporization, Henry's law constant, lethal dose, liquid viscosity, molar refraction, octanol-water partition coefficient, ozone-depletion potential, polarizability, refractive index, temperature sensitivity, vapor heat capacity, vapor pressure, vapor thermal conductivity, vapor viscosity, and water solubility.

SECTION II

PRIORITIZATION, GROUPING, AND PROPERTY ESTIMATION FOR CANDIDATES

A. GROUPING OF CHEMICAL CANDIDATES

At NMERI, candidate halocarbons have been divided into four classes based on toxicity and availability: Groups 1, 2, 3, and 4 (Reference 12). These groups correspond to near-, intermediate-, and long-term candidates and unacceptable chemicals. Group 1 (near-term) candidates are those chemicals that have been produced in bulk in the recent past, are now being produced, or are being developed for near-term bulk production, and for which significant toxicity studies, generally up to and including chronic studies, have been performed or are now in progress and indicate acceptable toxicity. Group 2 chemicals are expected to have low toxicities; however, limited toxicity information is available. Group 2 chemicals are often available in at least small (research) quantities. Group 3 (far-term) chemicals are expected to have very good or even superior fire extinguishment capabilities, but have little or no toxicity data available. Group 4 are all remaining chemicals that have been excluded from further consideration at this time because of high toxicity or undesirable physical or environmental properties.

To group and prioritize additional candidate agents and to confirm the prioritization to date, additional physical property evaluations are needed. In this section, physical property estimation is reviewed. Sections IV (fire suppression), VI (general physical properties), and VII (biological and toxicological indices) present discussions of specific prediction methodologies. Appendix A contains detailed information on prediction methods.

B. PHYSICAL PROPERTY PREDICTION

To develop and screen lists of candidate agents for given applications, values of key properties are required: boiling point, vapor pressure at room temperature, vapor heat

capacity, heat of vaporization, liquid density, and liquid or vapor viscosity. The significance of these properties to firefighting agents is discussed in detail in Reference 6. For initial screening, accuracy within 5 percent on most properties is sufficient. Agents that pass the initial screening can then be examined in greater detail, and experimental values of properties can be determined.

Unfortunately, information on physical and toxicological properties of many halocarbons is difficult or impossible to locate in the literature. For example, the property availability compiled from a comprehensive literature search for chemicals currently contained in the computerized NMERI HALOCARBON DATABASE of over 650 halocarbons is shown in Table 1.

TABLE 1. SURVEY OF AVAILABILITY OF LITERATURE DATA.

Property	Percent of Compounds for Which Property Has Been Reported
Boiling point	48
Liquid density	23
Refractive index	18
Vapor heat capacity	15
Heat of formation	14
Heat of vaporization	12
Other properties	< 10

Except for a few well-studied halocarbons such as methylene chloride, chloroform, carbon tetrachloride, and a handful of others, comprehensive sets of measurements of the physical properties of halocarbons are not readily available. Information on physical properties of halocarbons is widely scattered and often scanty. In fact, only 48 percent of the halocarbons in the NMERI HALOCARBON DATABASE have reported boiling points. As shown in Table 1, boiling point is the most commonly reported property, followed by liquid density and refractive index.

For purposes of ranking the attractiveness of each firefighting agent, properties can be prioritized into three categories—high, medium, and low. A suggested prioritization list is shown in Table 2. Such lists should, however, be treated cautiously. The prioritization may be highly dependent on application. Moreover, as requirements are better defined, less important properties may become more important. For example, water solubility would appear to be a relatively unimportant characteristic of a fire-extinguishing agent; however, molecular design to cause "rainout" may become increasingly important owing to concerns about atmospheric lifetime (Reference 11), and for such compounds, water solubility would become an exceedingly important parameter.

TABLE 2. PRIORITIZATION OF PROPERTIES FOR FIREFIGHTING.

Priority 1 (high)	Priority 2 (medium)	Priority 3 (low)
Anesthetic dose	Critical properties (P, V, T)	Bond strength
Atmospheric lifetime	Heat of reaction	Bioconcentration factor
Boiling point	Heat of vaporization	Dielectric constant
Carcinogenicity	Liquid viscosity	Heat of formation
Cardiac sensitivity	Liquid heat capacity	Henry's law constant
Fire suppression	Molar refraction	Liquid thermal conductivity
Global warming potential	Octanol-water partition coefficient	Polarizability
Lethal dose	Vapor thermal conductivity	Surface tension
Liquid density		Vapor viscosity
Ozone depletion potential		Water solubility
Temperature sensitivity		
Vapor heat capacity		
Vapor pressure		

C. DEVELOPMENT OF ESTIMATION METHODS

Although experimentally determined values of physical properties should be used when available, estimation methods become attractive when reliable measured values are unavailable and resources for determination do not exist (Appendix A). Important references are contained in the Appendix C list of Selected References on Prediction of Physical Properties (Appendix B). Numerous theoretical and empirical relationships exist among physical properties. If a theoretically-based correlation is not known, often an empirical correlation can be found (Appendix C). Estimation methods can be ranked in order of attractiveness; the most attractive are those based on close theoretical correlations that yield highly accurate and precise results and are easy to apply to a great number of compounds.

In general, the process of development of an estimation method involves the following steps:

1. Reviewing the literature for precedents
2. Compiling a data set
3. Developing of equation(s)
4. Fitting of parameters
5. For compounds with known values, comparing known and calculated values
6. Calculating values for other compounds with unknown values
7. Continuing to update data and revise algorithm as needed

For any estimation method, reliability must be assessed, propagation of errors in the calculations must be examined, and continuing comparison of estimated and experimental values must be carried out. The distinction between accuracy and precision must be emphasized here. Accuracy means having a value close to the "true" value. Precision means the degree of refinement of the measurement, as reflected in the number of significant figures. The accuracy is specified by the uncertainty of the method. For any estimation method, the reliability of the predictions must be known. One way to test the accuracy of the predictions made is to use the estimation method to generate values for which experimental data are available. Comparison of the predicted and experimental values yields a standard deviation (σ). If the standard deviation for a method is known,

the predictions made is to use the estimation method to generate values for which experimental data are available. Comparison of the predicted and experimental values yields a standard deviation (σ). If the standard deviation for a method is known, it can be estimated that a 68 percent chance exists that the true value lies within $\pm\sigma$ of the estimate, and a 96 percent probability that it lies within $\pm 2\sigma$.

Estimation methods can be grouped broadly into the categories of equations with solid theoretical foundations, quantum mechanical calculations, group additivity, molecular connectivity, corresponding states, and purely empirical correlations. The estimation methods discussed for each property are summarized in Table 3.

D. TOXICOLOGICAL INDICES

Since for some applications, toxicity is a screening technique few compounds will pass, and because of the high cost and time involved, it is especially desirable to be able to make accurate toxicity estimates. Significant progress has been made in the last few years on quantitative structure-activity relationships (QSARs). Several types of QSARs, based on molecular connectivity, octanol-water partition coefficients (K_{ow}), or linear solvation energy relationships (LSERs) exist (References 13 and 14). QSARs have been used to estimate lethal and anesthetic doses, bioconcentration factors, and reproductive toxicity in many species of fish and small aquatic organisms. Estimation methods have been devised to predict lethality and anesthetic potency in mice. In some cases, the same techniques used in QSARs can be applied to estimation of chemical and physical properties such as acidity and Henry's law constant. Previously published algorithms are summarized herein which correlate K_{ow} with bioconcentration factors, LC_{50} s for fish, daphnid, and mycid, and effective concentrations (EC_{50} s) for daphnid reproduction and inhibition of green algae photosynthesis (Reference 15). Methods of predicting toxicological parameters are discussed in Section VII of this report.

TABLE 3. SURVEY OF ESTIMATION METHODS FOR HALOALKANE PROPERTIES.

Property	Quantum Mechanics	Group Additivity	Molecular Connectivity	Empirical Correlation	Theoretical Equation	Corresponding States
Anesthetic dose		X	X	X		
Atmospheric lifetime		X				
Bioconcentration factor			X	X		
Bond strength	X	X				
Boiling point		X		X		X
Carcinogenicity			X			
Cardiac sensitization		X				
Critical pressure	X					
Critical temperature	X					
Critical volume	X					X
Dielectric constant	X					
Dipole moment	X					
Fire suppression conc.		X				
Global warming potential		X				
Heat of formation	X					
Heat of reaction	X					
Heat of vaporization				X		X
Henry's law constant			X			
Lethal dose		X		X		
Liquid density		X				X
Liquid heat capacity		X				X
Liquid thermal conductivity					X	X
Liquid viscosity		X		X		X
Molar refraction	X		X	X		
Octanol-water coefficient				X		
Ozone-depletion potential		X				
Polarizability	X					
Refractive index		X				
Surface tension						X
Temperature sensitivity	X					
Vapor heat capacity	X	X				X
Vapor pressure					X	X
Vapor thermal conductivity						X
Vapor viscosity		X				X
Water solubility			X	X		

E. TRENDS

For empirical correlations, this study examines trends in physical properties of well-studied, small fluorine-containing halocarbons. Some chemical series for evaluation of trends are proposed in Appendix C. The class of small fluorine-containing haloalkanes (those chemicals most likely to serve as halon replacements) possesses some unique physical, chemical, and toxicological properties. These properties include cleanliness, chemical stability, three-dimensional fire-extinguishing ability, and boiling points and vapor pressures in a range useful for many applications.

Exactly 69 one-carbon halomethanes are possible: 34 noniodinated and 35 iodine-containing. All possible one-carbon haloalkanes are listed in Table 4. Approximately half of these are known compounds. The possible noniodinated haloethanes number 217. Several thousand halopropanes are possible. Because of the large number of possible small haloalkanes, plus the fact that only a small percentage have properties reported in the literature, estimation techniques for properties of interest are essential.

F. GROUP 1 CANDIDATES

The Group 1 candidates are potential near-term agents; they are all available in bulk (either now, in the past, or in the anticipated near future) and have demonstrated low toxicity with significant toxicity testing completed. Although HCFC-123 and FC-5-1-14 (either neat or in blends) are proposed as near-term halon replacements, it must be recognized that none of the Group 1 agents offer the combination of excellent deliverability and extinguishment, low toxicity, and low environmental impact required for an ultimate halon alternative. Nevertheless, Group I near-term agents are the primary subject of this project. More effective, second-generation agents are discussed in Section V.

TABLE 4. LIST OF ALL POSSIBLE ONE-CARBON HALOCARBONS.

Halocarbon No.	Chemical Formula	Halocarbon No.	Chemical Formula	Halocarbon No.	Chemical Formula
10	CCl_4	20	CHCl_3	30	CH_2Cl_2
10B1	CBrCl_3	20B1	CHBrCl_2	30B1	CH_2BrCl
10B2	CBr_2Cl_2	20B2	CHBr_2Cl	30B2	CH_2Br_2
10B3	CBr_3Cl	20B3	CHBr_3	30B1I1	CH_2BrI
10B4	CBr_4	20B1I1	CHBrClI	30I1	CH_2ClI
10B1I1	CBrCl_2I	20B1I2	CHBrI_2	30I2	CH_2I_2
10B1I2	CBrClI_2	20B2I1	CHBr_2I	---	---
10B1I3	CBrI_3	20I1	CHCl_2I	31	CH_2ClF
10B2I1	CBr_2ClI	20I2	CHClI_2	31B1	CH_2BrF
10B2I2	CBr_2I_2	20I3	CHI_3	31I1	CH_2FI
10B3I1	CBr_3I	---	---	---	---
10I1	CCl_3I	21	CHCl_2F	32	CH_2F_2
10I2	CCl_2I_2	21B1	CHBrClF		
10I3	CClI_3	21B2	CHBr_2F	40	CH_3Cl
10I4	Cl_4	21B1I1	CHBrFI	40B1	CH_3Br
		21I1	CHClFI	40I1	CH_3I
11	CCl_3F	21I2	CHF_2I	---	---
11B1	CBrCl_2F	---	---	41	CH_3F
11B1I1	CBrClFI	22	CHClF_2		
11B1I2	CBrFI_2	22B1	CHBrF_2		
11B2	CBr_2ClF	22I1	CHF_2I		
11B2I1	CBr_2FI				
11B3	CBr_3F	23	CHF_3		
11I1	CCl_2FI				
11I2	CClFI_2				
11I3	CFI_3				
12	CCl_2F_2				
12B1	CBrClF_2				
12B2	CBr_2F_2				
12B1I1	CBrF_2I				
12I1	CClF_2I				
12I2	CF_2I_2				
13	CClF_3				
13B1	CBrF_3				
13I1	CF_3I				
14	CF_4				

Halon production will effectively end sometime in 1993, and, as yet, the search for halon replacements has not been completely successful. A large number of candidate replacement agents have been announced for commercialization (Table 5), and even more chemicals are under serious consideration. Yet, all of these "first-generation" agents have serious tradeoffs in one way or another.

TABLE 5. CANDIDATE HALON REPLACEMENTS FOR COMMERCIALIZATION.

Candidate	Chemical Formula	Primary Application
HBFC-22B1	CHF_2Br	Streaming
HCFC-123	CF_3CHCl_2	Streaming
HCFC-124	CF_3HCIF	Total-Flood
FC-3-1-10	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$	Total-Flood
FC-5-1-14	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	Streaming
HFC-23	CHF_3	Total-Flood
HFC-125	CF_3CHF_2	Total-Flood
HFC-227ea	$\text{CF}_3\text{CHF}_2\text{CF}_3$	Total-Flood
NAF S-III	Blend (primarily HCFC)	Total-Flood
NAF P	Blend (primarily CFC)	Streaming
Halotron I	Blend (primarily HCFC)	Streaming

SECTION III

LABORATORY-SCALE TESTING

NMERI has produced three different cup burners for laboratory-scale agent evaluation—full-scale, 5/8-scale, and 2/5-scale. The cup-burner design, procedures for use, and calibration are discussed in detail in Reference 7. The work cited shows that the 5/8-scale cup burner gives the most reproducible results, and this cup burner is the one usually employed in halon replacement work at NMERI.

Fifty-three halocarbons had been tested in the NMERI 5/8-scale cup burner by the date that technical work on this phase of the project was completed (April 1992). The materials were tested using n-heptane fuel and employing either liquid or gas injection procedures (Reference 7). The results are shown in Table 6 and are used in Section IV to further the development of an extinguishment algorithm.

TABLE 6. EXTINGUISHING CONCENTRATIONS, 5/8-SCALE CUP BURNER.

Halocarbon No.	Halon No.	Name	CAS No.	Density ^a (g/mL)	Ext. Conc. (%)
10	104	Tetrachloromethane	56-23-5	1.594(20)	7.61
11	113	Trichlorofluoromethane	75-69-4	1.464(30)	7.75
12	122	Difluorodichloromethane	75-71-8	1.13	7.64
12B1	1211	Bromochlorodifluoromethane	353-59-3	1.850(15)	3.22
13	131	Chlorotrifluoromethane	75-72-9	1.3	7.22
13B1	1301	Bromotrifluoromethane	75-63-8	1.499(30)	2.86
14	14	Perfluoromethane	75-73-0	1.317(-80)	13.79
20	103	Trichloromethane	67-66-3	1.483(20)	12.65
22	121	Chlorodifluoromethane	75-45-6	1.174(20)	11.60
22B1	1201	Bromodifluoromethane	1511-62-2	1.55(16)	4.41
23	13	Trifluoromethane	75-46-7	1.52(-100)	12.44
30	102	Dichloromethane	75-09-2	1.33	14.10
31	111	Chlorofluoromethane	593-70-4	1.27	20.03
32	12	Difluoromethane	75-10-5	1.204	8.75
113	233	1,2,2-Trichloro-1,1,2-trifluoroethane	76-13-1	1.56	6.19
114	242	1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	1.53	6.41
114B2	2402	1,2-Dibromo-1,1,2,2-tetrafluoroethane	124-73-2	2.16	2.12
115	251	1-Chloro-1,1,2,2,2-pentafluoroethane	76-15-3	1.57	6.28
115I1	25001	Pentafluoroiodoethane	354-64-3	---	2.09
116	26	Perfluoroethane	76-16-4	1.59(-78)	7.80
121	214	1-Fluoro-1,1,2,2-tetrachloroethane	354-14-3	1.549	7.77
122a	223	1,1-Difluoro-1,2,2-trichloroethane	354-21-2	1.54	6.33
123	232	2,2-Dichloro-1,1,1-trifluoroethane	306-83-2	1.462	6.25
123a	232	1,2-Dichloro-1,1,2-trifluoroethane	354-23-4	1.50	7.23
123aB1	2311	2-Bromo-2-chloro-1,1,1-trifluoroethane	151-67-1	---	3.12
123aB2	2302	2,2-Dibromo-1,1,1-trifluoroethane	354-30-3	2.22	1.88
123B2	2302	1,2-Dibromo-1,1,2-trifluoroethane	354-04-1	2.274	2.01

^aAt 25 °C unless temperature in °C is stated in parentheses.^bNot applicable.^cNot a haloalkane, and not used in developing fire suppression algorithm.

TABLE 6. EXTINGUISHING CONCENTRATIONS, 5/8-SCALE CUP BURNER (CONCLUDED).

Halocarbon No.	Halon No.	Name	CAS No.	Density ^a (g/mL)	Ext. Conc. (%)
123bB1	2311	1-Bromo-2-chloro-1,1,2-trifluoroethane	354-06-3	1.86	3.17
124	241	2-Chloro-1,1,1,2-tetrafluoroethane	2837-89-0	1.38	8.15
124B1	2401	2-Bromo-1,1,1,2-tetrafluoroethane	124-72-1	---	2.80
125	25	Pentafluoroethane	354-33-6	1.23	9.41
130a	204	1,1,1,2-Tetrachloroethane	630-20-6	1.54	7.96
132b	222	1,2-Dichloro-1,1-difluoroethane	1649-08-7	1.41	7.85
133a	231	2-Chloro-1,1,1-trifluoroethane	75-88-7	1.389	7.59
134	24	1,1,2,2-Tetrafluoroethane	359-35-3	---	11.20
134a	24	1,1,1,2-Tetrafluoroethane	811-97-2	---	10.47
141b	212	1,1-Dichloro-1-fluoroethane	1717-00-6	1.23	12.25
142B1	2201	2-Bromo-1,1-difluoroethane	359-07-9	1.82	4.17
216ab	362	1,2-Dichloro-1,1,2,3,3,3-hexafluoropropane	661-97-2	1.59	4.89
217I1	37001	1,1,1,2,3,3,3-heptafluoro-2-iodopropane	677-69-0	---	3.15
217jbI1	37001	1,1,2,2,3,3,3-heptafluoro-1-iodopropane	754-34-7	---	3.04
218ca	38	Perfluoropropane	76-19-7	---	6.11
270	302	1,3-Dichloropropane	142-28-9	1.19	5.46
270f	302	1,2-Dichloropropane	78-87-5	1.16	4.64
272ea	32	1,2-Difluoropropane	62126-90-3	---	5.60
C-318	48	Perfluorocyclobutane	115-25-3	1.48	7.19
5-1-13I1	6-13-001	Tridecafluoro-1-iodohexane	355-43-1	---	3.35
5-1-14	6-14	Perfluorohexane	355-42-0	1.7	4.42
6-1-16	7-16	Perfluoroheptane	355-57-9	---	3.99
7-1-16	8-16	Perfluoro-1,3-dimethylcyclohexane	335-27-3	1.83	3.45
7-1-17B1	8-17-0-1	1-Bromoperfluorooctane	423-55-2	---	2.44
^b	7-14	Perfluoro(methylcyclohexane)	355-02-2	1.79	4.30
^b	^b	Chloropentafluorobenzene ^c	344-07-0	---	5.40

^aAt 25 °C unless temperature in °C is stated in parentheses.

^bNot applicable.

^cNot a haloalkane, and not used in developing fire suppression algorithm.

SECTION IV

FIRE EXTINGUISHMENT PREDICTION

An improved algorithm has been developed for estimating the fire-suppression concentrations of haloalkanes based on molecular formula. The previous NMERI fire suppression prediction algorithm was based on fitting of published data on 11 compounds to the formula developed by Hirst and Booth (Reference 16). The basic prediction formula employed a parameterized fit to the molecular formula developed using regression techniques. The formula predicted the concentration necessary to extinguish flames in a cup burner using *n*-heptane fuel. The formula has the functional form

$$\log F = -A \log(BN_F + CN_{Cl} + DN_{Br}) + E \quad (1)$$

where *F* is the cup-burner fire suppression concentration in percent, *N_F*, *N_{Cl}*, and *N_{Br}* are the numbers of fluorine, chlorine, and bromine atoms in the molecule, and *A*, *B*, *C*, *D*, and *E* are the estimated parameters of regression. In earlier work, this equation was redefined to include hydrogen atoms, and the parameters were recalculated (Reference 11). Here, the equation is further examined.

Equation (1) is equivalent to

$$F = 10^E / (BN_F + CN_{Cl} + DN_{Br})^A \quad (2)$$

The best fit ($R^2 = 0.941$ for 11 compounds) for Equations (1) and (2) was given by $A = 0.811$, $B = 0.685$, $C = 2.953$, $D = 12.350$, and $E = 1.558$ (Reference 11).

To develop a new algorithm, the formula in Equation (1) was expanded to examine explicitly the effects of carbon, hydrogen, and iodine atoms and CF_3 groups. The functional form is shown in Equation (3).

$$F = 1 / (A + BN_C + CN_H + DN_{Br} + EN_{Cl} + FN_F + GN_{CF_3} + HN_I) \quad (3)$$

It was found that use of an exponent (e.g., A in Equations (1) and (2)) did not improve the quality of fit in Equation (3), so no exponent was used. Furthermore, the constant corresponding to E in Equation (1) and 10^E in Equation (2) was unnecessary because the constant and coefficients in the denominator of Equation (3) were scaled to incorporate the effect of a constant in the numerator.

Regression analysis is used to fit parameters for equations such as Equation (3). Simple least-squares estimation of the regression coefficients, however, suffers from several drawbacks. One critical problem is that one or two outlying values can greatly distort the coefficients. If only one or two independent variables are used, scatter plots can be used to find outlying values. However, if several independent variables are used, it is difficult to identify outlying data by plotting. Using successive iterations, robust regression techniques find these outlying points and minimize their effects on the parameters. During robust regression, at every iteration each observation is assigned a weight by one of three robustifying functions, for example, the Least Absolute Deviation, Andrew's Sine, and Tukey's Biweight. The functions assign small or zero values to observations that differ dramatically from the equation and larger values to observations that are in closer agreement. Iteration continues until the changes per iteration in the regression parameters or weights are very small.

Data were fitted for 51 compounds for which extinguishment concentrations were measured on the 5/8-scale cup burner at NMERI (Table 5). The multiple-regression analysis was carried out using the Number Cruncher Statistical System (NCSS). The method used the robust Andrew's Sine function; 22 iterations were performed until the maximum decrease in beta values per iteration fell below 1 percent. Two other fitting methods were tested (Least Absolute Deviation and Tukey's Biweight) but both of these were slightly inferior to Andrew's Sine in quality of fit.

The best-fit parameterized equation is shown in Equation (4). The quality of fit was excellent, with $R^2 = 0.978$ for 51 compounds (44 degrees of freedom).

$$F = 1/(0.07231 + 0.06009N_C - 0.01440N_H + 0.1882N_{Br} + 0.03785N_{CF_3} + 0.00620N_{Cl} - 0.0209N_F + 0.03785N_{CF_3} + 0.1271N_I) \quad (4)$$

Here, N_x is the number of x atoms or groups in the molecule (i.e., C, H, Br, Cl, F, or I atoms or CF_3 groups).

The magnitudes and signs of the coefficients are in agreement with several expectations. For example, larger molecules (with more carbon atoms) have more degrees of freedom and higher vapor heat capacities than smaller molecules, and, therefore, provide greater physical extinguishment. This reasoning agrees with the relatively large positive coefficient for carbon. Bromine is the most significant contributor to chemical extinguishment, closely followed by iodine. The way this algorithm is set up, the contribution of a CF_3 group is the sum of the effects of one carbon atom, three fluorine atoms, and one CF_3 group:

$$0.0352 = 0.06009 + 3(-0.0209) + 0.03785 \quad (5)$$

According to this parameterization, an iodine atom is about 68 percent as effective in extinguishment as a bromine atom ($0.1271/0.1882 = 0.68$). An additional carbon atom contributes 32 percent of the effect of a bromine atom ($0.06009/0.1882 = 0.32$). The effect of a CF_3 group is 19 percent of the effect of a bromine atom ($0.0352/0.1882 = 0.19$). From the magnitudes and signs of the coefficients, the order of contributions of chemical features to extinguishment is (from greatest positive contribution to extinguishment to greatest negative): $Br > I > C > CF_3 > Cl > H > F$.

As shown by the small absolute values of the coefficients for Cl, H, F, and CF_3 groups, these items could be left out of the model altogether without significantly lowering the quality of fit. However, these groups were left in for maximum accuracy and maximum differentiation of structures.

SECTION V

SECOND-GENERATION AGENTS

Halon replacements require four characteristics: a low global environmental impact (i.e., low-ozone depletion potential [ODP] and low global warming potential [GWP]), acceptable toxicity, cleanliness and volatility, and effectiveness. Though it is very easy to find candidate replacements that meet any three of these criteria, it has been difficult to find agents that meet all four. Certainly, none of the first-generation agents has both a low ODP/GWP and an effectiveness equal to that of the present halons across all applications.

Thus serious consideration must be given to a second generation of candidate agents—materials that are highly effective, yet have low global environmental impacts. Most of the past development of low-ODP agents has been based on a single idea: the elimination of the ozone-depleting bromine found in all of the present halons. Yet, it is bromine that gives existing halons their high effectiveness. Indeed, nearly all of the first-generation candidates contain no bromine (an exception being HBFC-22B1, which has a high ODP and which will be regulated in the future). On the other hand, second-generation agents contain bromine (or iodine, which is nearly equally effective) but also have a low ODP. The combination of bromine and a low ODP is accomplished by designing molecules that are removed from the atmosphere before they can contribute significantly to environmental problems.

Three families of chemicals are now under consideration. (1) The bromofluoroalkenes are compounds that rapidly react with atmospheric hydroxyl free radical so that their lifetime and, therefore, ODP/GWP are essentially zero. (2) The fluoroiodocarbons also have short atmospheric lifetimes because they are rapidly photolyzed by sunlight. (3) Finally, the polar-substituent bromocarbons, are partially water soluble, so that they are removed from the atmosphere by rainout. Some examples of the first two types of compounds are presented in Tables 7 through 9.

It must be pointed out that first-generation, rather than second-generation, candidates were emphasized in the project tasking. Nevertheless, second-generation candidates hold the only promise of replacement agents as effective as the present halons.

TABLE 7. SELECTED ALKENE SECOND-GENERATION CANDIDATES.

Formula	Name	BP (°C)	CAS No.
$\text{CH}_2=\text{CH}-\text{CF}_2\text{Br}$	1-bromo-1,1-difluoro-2-propene	42	420-90-6
$\begin{array}{c} \text{CBrF}_2 \\ \\ \text{CH}_2=\text{CH}-\text{CF}-\text{CF}_3 \end{array}$	3-(bromodifluoromethyl)-3,4,4,4-tetrafluoro-1-butene	79.5	2546-54-5
$\text{BrCH}=\text{CH}-\text{CF}_3$	1-bromo-3,3,3-trifluoro-1-propene	33	460-33-3
$\text{CH}_2=\text{CH}-\text{CF}_2\text{CF}_2\text{Br}$	4-bromo-3,3,4,4-tetrafluoro-1-butene	55	18599-22-9
$\text{CH}_2=\text{CBr}-\text{CBrF}_2$	2,3-dibromo-1,1-difluoro-2-propene	100	677-35-0
$\text{CH}_2=\text{CH}-\text{CClF}-\text{CF}_2\text{Br}$	4-bromo-3-chloro-3,4,4-trifluoro-1-butene	96	374-25-4
$\text{BrCH}=\text{CBr}-\text{CF}_3$	1,2-dibromo-3,3,3-trifluoro-1-propene	96	431-22-1
$\text{CF}_2\text{CH}-\text{CF}_2\text{Br}$	3-bromo-1,1,3,3-tetrafluoro-1-propene	35	-----

TABLE 8. FLUOROIODOCARBONS IN ORDER OF INCREASING BOILING POINT.

Formula	Name	Halocarbon No.	Halon No.	CAS No.
CF ₃ I	trifluoroiodomethane	13I1	13001	2314-97-8
CF ₃ CF ₂ I	pentafluoroiodoethane (perfluoroethyl iodide)	115I1	25001	354-64-3
CHF ₂ I	difluoroiodomethane	22I1	12001	1493-03-4
CF ₃ CF ₂ CF ₂ I	1,1,2,2,3,3,3-heptafluoro- 1-iodopropane	217jbI1	37001	754-34-7
CH ₂ FI	fluoroiodomethane	31I1	11001	373-53-5
CF ₂ I ₂	difluorodiiodomethane	12I2	12002	1184-76-5
CF ₃ CF ₂ CF ₂ CF ₂ I	1,1,2,2,3,3,4,4,4- nonafluoro-1-iodobutane (perfluoro-n-butyl iodide)	319I1	49001	423-39-2
CF ₂ ICHF ₂	1,1,2,2-tetrafluoro-1- iodoethane	124aI1	24001	3831-49-0
CF ₂ ICH ₂ F	1,1,2-trifluoro-1-iodoethane	133bI1	23001	20705-05-9
CF ₂ ICH ₃	1,1-difluoro-1-iodoethane	142bI1	22001	420-47-3
CF ₂ ICF ₂ CHF ₂	1,1,2,2,3,3-hexafluoro-1- iodopropane	226cbI1	36001	431-90-3
CF ₂ ICHFCF ₃	1,1,1,2,3,3-hexafluoro-3- iodopropane	226eaI1	36001	58706-58-4
CF ₂ ICF ₂ CH ₂ F	1,1,2,2,3-pentafluoro-1- iodopropane	235ccI1	35001	371-75-5
CF ₂ ICHFCHF ₂	1,1,2,3,3-pentafluoro-1- iodopropane	235ebI1	35001	58706-52-8
CF ₂ ICH ₂ CF ₃	1,1,1,3,3-pentafluoro-3- iodopropane	235faI1	35001	58777-36-9
CF ₂ ICHFCCH ₂ F	1,1,2,3-tetrafluoro-1- iodopropane	244ecI1	34001	58706-49-3
CF ₂ ICH ₂ CHF ₂	1,1,3,3-tetrafluoro-1- iodopropane	244fbI1	34001	58777-34-7
CH ₂ IC(CF ₃) ₃	1,1,1,3,3,3-hexafluoro-2- (iodomethyl)-2-(trifluoromethyl)- propane	--	59001	79792-31-7
CF ₂ IC(CF ₃) ₃	2-(difluoroiodomethyl)-1,1,1,3,3,3- hexafluoro-2-(trifluoromethyl)- propane	--	5-11-001	71076-45-4

TABLE 9. PROPERTIES OF FLUOROIODOCARBONS.

Formula	Name	Molecular Wt.	Boiling Pt. (°C)	Vapor Pres. lb/in. ² abs	Density (g/mL)	Freezing Pt. (°C)
CF ₃ I	trifluoroiodomethane	195.9	-23	87.2	2.36	--
CF ₃ CF ₂ I	pentafluoroiodoethane (perfluoroethyl iodide)	245.9	13	13.9	2.07	--
CHF ₂ I	difluoroiodomethane	177.9	22	17.7	3.24	-122
CF ₃ CF ₂ CF ₂ I	1,1,2,2,3,3,3-heptafluoro-1-iodopropane	295.9	41		2.06	-95
CH ₂ FI	fluoroiodomethane	159.9	53	0.58	2.37	-33
CF ₂ I ₂	difluorodiiodomethane	303.8	80	--	v. high	--
CF ₃ CF ₂ CF ₂ CF ₂ I	1,1,2,2,3,3,4,4,4-nonafluoro-1-iodobutane (perfluoro-n-butyl iodide)	345.9	67	--	2.01	--
CF ₂ ICHF ₂	1,1,2,2-tetrafluoro-1-iodoethane	227.9	--	--	--	--
CF ₂ ICH ₂ F	1,1,2-trifluoro-1-iodoethane	209.9	--	--	--	--
CF ₂ ICH ₃	1,1-difluoro-1-iodoethane	191.9	--	--	--	--
CF ₂ ICF ₂ CHF ₂	1,1,2,2,3,3-hexafluoro-1-iodopropane	277.9	--	--	--	--
CF ₂ ICHFCF ₃	1,1,1,2,3,3-hexafluoro-3-iodopropane	277.9	--	--	--	--
CF ₂ ICF ₂ CH ₂ F	1,1,2,2,3-pentafluoro-1-iodopropane	259.9	--	--	--	--
CF ₂ ICHFCHF ₂	1,1,2,3,3-pentafluoro-1-iodopropane	259.9	--	--	--	--
CF ₂ ICH ₂ CF ₃	1,1,1,3,3-pentafluoro-3-iodopropane	259.9	--	--	--	--
CF ₂ ICHFCCH ₂ F	1,1,2,3-tetrafluoro-1-iodopropane	241.9	--	--	--	--
CF ₂ ICH ₂ CHF ₂	1,1,3,3-tetrafluoro-1-iodopropane	241.9	--	--	--	--
CH ₂ IC(CF ₃) ₃	1,1,1,3,3,3-hexafluoro-2-(iodomethyl)-2-(trifluoromethyl)-propane	359.9	--	--	--	--
CF ₂ IC(CF ₃) ₃	2-(difluoroiodomethyl)-1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-propane	395.9	--	--	--	--

SECTION VI

PHYSICAL PROPERTY PREDICTIONS

A. INTRODUCTION

The effectiveness of a firefighting agent depends upon agent deliverability, heat-removal ability (physical extinguishment), and radical trapping ability (chemical extinguishment). Properties relating to deliverability include vapor pressure, density, and viscosity. The vapor pressure (which is related to the boiling point and heat of vaporization) determines whether an agent is delivered as a liquid or gas and how quickly its vapor contacts the flames. The density and viscosity of an agent affect its flow patterns through nozzles; density also affects the volumes of storage containers needed. Properties relating to heat removal ability include vapor heat capacity, heat of vaporization, and heat of reaction. A molecule with a high vapor heat capacity (corresponding in general to a large molecule with many bonds to absorb vibrational energy) removes heat more effectively. A higher heat of vaporization will remove more heat but will require a longer time for evaporation and for contact with the flames. A high negative heat of reaction means that the agent releases heat as it reacts, encouraging the fire; however, this is a minor factor and some molecules may need this to break down quickly to provide chemical extinguishment (radical trapping). Properties related to radical-trapping ability include types of atoms present and bond strengths. Bromine or iodine atoms catalytically aid the recombination of flame free radicals. If these atoms are weakly bonded in the parent molecule, they will be released more easily in flames. It has been suggested that the excellent extinguishment by Halon 1301 (CF_3Br) may be aided by the weak C-Br bond in the ionized form of the molecule (CF_3Br^+) (References 17 and 18).

B. GROUP ADDITIVITY

Group contribution techniques often provide simple, convenient methods for physical property estimation. These empirical methods are based on the assumption that a particular

physical property can be considered to be made up of contributions from the constituent atoms and groups. Table 10 lists all possible bond types and noniodine-containing substituent groups encountered in unbranched acyclic haloalkanes. The numerical values of these contributions are determined by examining experimental data. Detailed group contribution methods have been developed for estimation of several properties, including boiling point, heat of formation, and vapor heat capacity (References 19 through 21). As one example, molar refraction provides an approximate measure of the actual total volume (without free space) occupied by the molecules in one mole of the substance. For a very large number of compounds molar refraction may be approximated for a molecule by adding the contributions of the constituent atoms. A linear relationship has been reported between the molar refraction and $\log K_{ow}$ (Reference 22). Several other properties also correlate with molar refraction.

TABLE 10. BOND TYPES AND NONIODINATED ONE-CARBON SUBSTITUENTS.

Types of bonds	Types of one-carbon substituents (excluding iodine)	
	Terminal (trisubstituted)	Internal (disubstituted)
C-C	-CH ₃ , -CF ₃ , -CCl ₃ , -CBr ₃	-CH ₂ -, -CF ₂ -, -CCl ₂ -, -CBr ₂ -
C-H	-CClF ₂ , -CCl ₂ F, -CBrF ₂	-CClF-, -CBrF-, -CBrCl-
C-F	-CBr ₂ F, -CBrCl ₂ , -CBr ₂ Cl,	-CHF-, -CHCl-, -CHBr-
C-Cl	-CBrClF, -CHF ₂ , -CHCl ₂ ,	
C-Br	-CHBr ₂ , -CHClF, -CHBrF,	
C-I	-CHClBr, -CH ₂ F, -CH ₂ Cl,	
	-CH ₂ Br	

One possible problem with group additivity schemes is that an ambiguity problem may arise: the same molecule can be constructed out of different sets of groups and the resulting estimated values may differ slightly. In these cases the groups should be defined as closely as possible to the manner in which the original algorithm was developed.

C. CORRESPONDING STATES

Estimation methods, based on corresponding states, are founded on the empirical observation that if pressure-volume-temperature (PVT) data are plotted for many compounds using reduced values, the curves are very similar. A reduced value is the value divided by the critical value. By using the reduced values of pressure, volume, and temperature, most of the compound-dependent information is removed. A small number of parameters can then be used to estimate PVT information. These parameters are more related to the process occurring than the compound involved.

D. QUANTUM MECHANICAL CALCULATIONS

Quantum mechanical calculations provide estimates of properties that depend directly on the energy states and electron distributions (intramolecular interactions) in a molecule. These properties include bond strength, dipole moment, polarizability, and bond vibration frequencies. From these basic properties, more macroscopic properties such as dielectric constant, vapor heat capacity, infrared spectra and temperature sensitivity can be calculated.

The object of the quantum mechanical approach is to solve the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (6)$$

where $\hat{H}$ is the quantum mechanical Hamiltonian operator given by

$$\hat{H} = -(\hbar^2/2m)\nabla^2 + \hat{V} \quad (7)$$

In Equation (7), ∇^2 is the differential operator $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, $\hat{V}$ is the appropriate potential energy operator, and m is the mass of the system being described.

The linear operator $\hat{H}$ acts on a function $\Psi(r)$ to return the function multiplied by a scalar quantity E , which in this case is the total energy of the system. Equations of this type are called eigenvalue equations and, in general, contain a number of eigenvalues E and eigenfunctions Ψ that satisfy the equation. The problem is to solve the differential equation for Ψ subject to the appropriate boundary conditions. Physically observable properties are derived from the resulting solutions Ψ and E . If the equation could be solved accurately for polyatomic molecules, virtually all physical and chemical properties of the molecules could be calculated. However, the Schrödinger equation can be solved exactly only for one-electron systems. In all other cases approximations must be introduced. In practice these approximations make calculations to chemical standards either inadequate or too costly. One approach is to introduce selected experimental data and adjustable parameters into the Schrödinger equation to improve the speed and accuracy of the calculations; this approach is the semiempirical method. Work in this program has employed the MOPAC suite of programs (Reference 23) to calculate bond strengths, heats of formation and reaction, dipole moments, dielectric constants, and polarizabilities for all one-carbon and selected two-carbon haloalkanes.

The approach employed is a modification of the widely used technique of approximating the multiple-electron wave functions ψ as a linear combination of one-electron functions φ_k , the collection of which is known as the basis set:

$$\psi = \sum c_k \varphi_k \quad (8)$$

The coefficients c_k are chosen to satisfy the variational principle which says that if an approximate energy $\bar{E}$ is calculated from the expression

$$\bar{E} = (\int \psi^* \hat{H} \psi d\tau) / (\int \psi^* \psi d\tau) \quad (9)$$

the resulting $\tilde{E}$ will always be greater than the "true" energy E_{true} . Thus the c_k are chosen to minimize Equation (9). Here, ψ^* is the complex conjugate of ψ , and $d\tau$ is the appropriate differential element. Minimization occurs when the following matrix equation is satisfied:

$$HC = \tilde{E}SC \quad (10)$$

The Hamiltonian matrix H has the elements

$$H_{ij} = \int \varphi_i^* \hat{H} \varphi_j d\tau \quad (11)$$

and the overlap matrix S has elements

$$S_{ij} = \int \psi_i^* \psi_j d\tau \quad (12)$$

When the eigenvalues $\tilde{E}_i$ for Equation (10) are obtained, each value i corresponds to the energy of the i -th state and the column C_i contains the coefficients that give the wave function for state i , ψ_i , as a linear combination of the φ_k .

Although this treatment gives qualitatively correct results, serious deficiencies exist that prevent calculations from giving "chemical" accuracy. The root of the problem is the use of one-electron basis functions φ_k in a multiple-electron system. To produce the desired accuracy for any physical property it is necessary to account for electron-electron interaction. It has been found to be useful in this regard to consider the many-electron Hamiltonian operator as being approximated by a modified many-electron Hamiltonian-like operator $\hat{H}^F$, which is written as a sum of effective one-electron Hamiltonian operators

$$\hat{H}^F = \sum_p \left(-(\hbar^2/2m) \nabla_p^2 + \hat{V}(p) \right) \quad (13)$$

The crucial factor here is the effective potential $\hat{V}(p)$ in that it is the potential experienced by one electron in the average field of all the other electrons. Determination of this potential depends on a prior knowledge of the wave functions φ_i . In practice, an estimate is used and the wave function of Equation (8) is iteratively refined to satisfy the variational principle. This is called the self-consistent field (SCF) approach.

The significant differences among various quantum mechanical treatments have to do with how the basis functions φ_i are chosen and how integrations involving them are performed. Many alternative choices are available (Reference 24). For the quantum mechanical calculations reported here the MINDO/3 (References 25 and 26) and AM1 (Reference 27) parameterizations of the φ_i and the integrals were used. This is a semiempirical method in that experimental data are employed for evaluation of, among others, resonance integrals such as Equation (8). Furthermore, the very difficult and time-consuming part of the SCF calculations, the evaluation of a large number of electron repulsion integrals, is reduced by various degrees of omission. For both of these methods, MINDO/3 and AM1, parameterization was optimized to give the best possible values for ground state properties of molecules, especially geometries, heats of formation, dipole moments and vibrational frequencies. AM1 appears to give more reliable estimates of activation barriers for reactions than do other semiempirical approaches (Reference 27). The quantum mechanical calculations reported here were produced by the MOPAC suite of programs (Reference 23), which contains the MINDO/3, MNDO and AM1 parameterizations in alternative form.

Descriptions of how physical properties are calculated from the approximate solutions to the Schrödinger equation are given in the discussions of those properties in Appendix A.

E. MOLECULAR CONNECTIVITY

The term "molecular connectivity" was adopted by Kier and Hall in 1975 to describe the use of indices based on molecular structure (Reference 28). Molecular connectivity is a structure-based approach to biological QSAR analysis and estimation of physical properties (References 13, 14, and 28). At a molecular level, structural information includes (1) the total number of atoms, (2) the number of different types of atoms, and (3) the bonding arrangement of atoms. Molecular connectivity indices are intermediate in complexity between a simple count of atoms and a quantum mechanical description. In this method, chi index values are calculated based on electron and orbital counts, incorporating information about topology and electronic structure. The identities of atoms and their connections constitute the topology of the molecule; three-dimensional aspects such as size, shape, volume, and surface area are called molecular topography. The bonding scheme (topology) determines the three-dimensional geometry. Only covalent bonds are considered, and hydrogen atoms are not shown.

A chemical structure can be represented either as a connection matrix or as a distance matrix. A connection matrix shows which atoms are covalently bonded to one another. For example, for *n*-pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) the connection matrix is

0	1	0	0	0
1	0	1	0	0
0	1	0	1	0
0	0	1	0	1
0	0	0	1	0

This matrix was arrived at by placing a "1" where two atoms are bonded and a "0" where they are not. Each column (or row; these matrices are symmetrical about the diagonal) represents one carbon atom, so Carbon 1 is bonded to Carbon 2 only. Carbon 2 is bonded to both Carbons 1 and 3. Carbon 3 is bonded to Carbons 2 and 4. Carbon 4 is bonded to

Carbons 3 and 5, and Carbon 5 is bonded only to Carbon 4. Once the set of connections has been represented in matrix form, certain information can be extracted easily. For example, the number of neighboring atoms connected to a given atom can be found by adding up the nonzero entries in the row (or column) corresponding to that atom. This quantity is called the vertex degree or valence, abbreviated δ_i for atom i , and is equal to the number of sigma bonds involving that atom exclusive of bonds to hydrogen.

The same information can also be represented in a distance matrix. For example, for n -pentane the distance matrix is

0	1	2	3	4
1	0	1	2	3
2	1	0	1	2
3	2	1	0	1
4	3	2	1	0

In this case the entry represents the distance (in number of bonds or, equivalently, number of atoms) to the other atoms. For example, Carbon 1 (represented in the first row or, equivalently, column) is zero distance from itself, one bond or atom removed from Carbon 2, two bonds or atoms away from Carbon 3, three from Carbon 4, and four from Carbon 5.

The method has been extended to account for heteroatoms, unsaturation, and extended bond analysis. For heteroatoms the δ value is obtained by adding up the number of adjacent nonhydrogen-bonded atoms plus all pi and lone pair electrons.

The simplest form of the index is abbreviated using the Greek letter chi and the superscript 1 to denote that the index is for a one-bond dissection of the molecule, $^1\chi$. To compute this index, the structural formula is written down as a molecular skeleton in which all atoms are identical and without hydrogen atoms. Each carbon atom is then assigned a whole number for the number of adjacent bonded nonhydrogen atoms. This count of adjacent bonded nonhydrogen atoms is called the delta value, δ . The molecular skeleton is

dissected into bonds, each described by the two carbon atoms, i and j , forming the bond. A value for each bond is computed using the Randic algorithm $(\delta_i \delta_j)^{-0.5}$. The first-order molecular connectivity index is simply the sum of these values.

$${}^1\chi = \sum (\delta_i \delta_j)^{-0.5} \quad (14)$$

For this index, heteroatoms are treated like carbon atoms, and hydrogen atoms bonded to heteroatoms are ignored. The first-order index does not fully describe a molecule containing heteroatoms, since the identities of the heteroatoms have not been specified. To include this information, higher-order indices are calculated. For the second order index, the molecular skeleton is dissected into all two-contiguous bond fragments. A term is computed for each two-bond (three-atom) fragment, and the sum of these terms yields the second-order molecular connectivity index, ${}^2\chi$.

$${}^2\chi = \sum (\delta_i \delta_j \delta_k)^{-0.5} \quad (15)$$

Higher order indices are possible by dissection of the molecule into all possible fragments containing m bonds (or $m+1$ contiguous atoms) and summation to give an ${}^m\chi_p$ index, where the subscript p denotes a contiguous path fragment.

The ability to treat heteroatoms has elevated the usefulness of molecular connectivity tremendously, making it a powerful structural description capable of analyzing structure-activity relationships among numerous molecules. Treatment of heteroatoms is achieved by the appropriate choice of delta value. To do this, a new type of delta value is defined: the valence delta, δ^v . For heteroatoms, the valence delta value is obtained by adding the number of adjacent bonded atoms (excluding hydrogen) plus the number of all pi and nonbonded electrons. For example, an oxygen atom in an alcohol (ROH) has $\delta^v_{OH} = 5$, from one bonded carbon atom and four nonbonded electrons. Another way to express the formula for valence delta for heteroatoms is

$$\delta^v = Z^v - h \quad (16)$$

where δ^v is the valence delta, Z^v is the number of valence electrons and h is the number of hydrogen atoms suppressed. This calculation of valence delta applies for unsaturated compounds as well as those containing heteroatoms. For an alkane, $\delta^v = \delta$. Table 11 lists valence delta values for sp^3 hybridized carbon and fluorine.

TABLE 11. VALENCE DELTA VALUES FOR SP^3 CARBON AND FLUORINE.

Atom	Number of H atoms	Adjacent atoms δ	Valence electrons	Pi electrons	Lone pair electrons	δ^v
C	3	1	4	0	0	1
C	2	2	4	0	0	2
C	1	3	4	0	0	3
C	0	4	4	0	0	4
F	0	1	7	0	6	7

Valence delta values describe the electronic structures of the skeletal atoms in molecules. Simple delta is a count of electrons in sigma orbitals; valence delta is a count of all valence electrons. Both types of delta values exclude electrons in bonds to hydrogen atoms. This approach is satisfactory in considering second row atoms such as C and F. In considering higher row atoms such as Cl, Br, and I, however, account must be taken of non-valence or core electrons. These core electrons influence both the sizes of the atoms and such properties as ionization potential and electron affinity. To account for both valence and core electrons, the valence delta value can be calculated according to Equation (17).

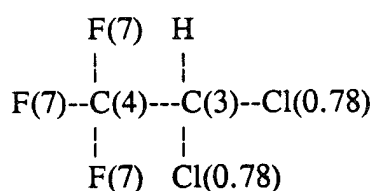
$$\delta^v = (Z^v - h) / (Z - Z^v - 1) \quad (17)$$

In the cases of second-row elements such as C and F, the denominator of this expression is 1. The numerator, denominator, and valence delta values calculated for Cl, Br, and I using Equation (17) are shown in Table 12.

TABLE 12. VALENCE DELTA VALUES FOR CHLORINE, BROMINE, AND IODINE.

Atom	$Z^v - h$	$Z - Z^v - 1$	δ^v
Cl	7	9	0.78
Br	7	27	0.26
I	7	47	0.16

The procedure for assigning $^1\chi^v$ indices, then, consists of assigning δ^v values to all atoms, specifying pairs of atoms in a first-order bond dissection, then summing up the contributions from pairs of atoms according to Equation (14). As an example, consider HCFC-123, 2,2-dichloro-1,1,1-trifluoroethane. The valence delta values for each non-hydrogen atom are shown in parentheses after the atom.



To calculate the first-order molecular connectivity, $^1\chi$, pairs of δ^v values are written for each adjacent pair of nonhydrogen atoms. In this case the pairs are

(4,7) (4,7) (4,7) (4,3) (3, 0.78) (3, 0.78)

The inverses of the square roots of the products of these pairs are then summed according to Equation (18).

$${}^1\chi^v = 3(4 \times 7)^{-0.5} + (4 \times 3)^{-0.5} + 2(3 \times 0.78)^{-0.5} = 3(0.189) + 0.289 + 2(0.654) = 2.164 \quad (18)$$

Terms from the larger atoms (Cl, Br, I) will dominate the indices because of their low δ^v values.

To calculate a second-order connectivity index, all contiguous three-atom segments (excluding hydrogen) must be considered. In the case of HCFC-123, nine such segments exist: three F-C-F, three F-C-C, two C-C-Cl, and one Cl-C-Cl. These groups give (respectively) the sets of δ^v values (7,4,7), (7,4,3), (4,3,0.78), and (0.78,3,0.78). Summing the inverse square roots of the product of each set of three to obtain the second-order connectivity index gives

$$\begin{aligned} {}^2\chi^v &= 3(7 \times 4 \times 7)^{-0.5} + 3(7 \times 4 \times 3)^{-0.5} + 2(4 \times 3 \times 0.78)^{-0.5} + (0.78 \times 3 \times 0.78)^{-0.5} \\ &= 3(0.071) + 3(0.109) + 2(0.327) + 0.740 \\ &= 1.934 \end{aligned} \quad (19)$$

F. EMPIRICAL CORRELATIONS

In related series of compounds many properties show smoothly-curving trends, and many pairs of properties show empirical correlations. Among small haloalkanes numerous series of related chemicals exist. Forty series involving one-carbon compounds have been developed. Each series can be described by two phrases, one describing which atom(s) are being substituted on the parent compound, and one describing the initial and final molecular formulas for the series. For example, the series CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 can be described as a series with one carbon atom and one chlorine atom, successively replacing three hydrogen atoms with three chlorine atoms, abbreviated C1Cl1 H3 TO Cl3. Obviously

many other series are possible. In series of related haloalkanes, we have found correlations of molecular weight with density, dielectric constant, dipole moment, heat of vaporization, and vapor heat capacity. More accurate estimates of the heat of vaporization can be made using knowledge of the vapor pressure-temperature relationship for the compound. Several correlations have been proposed.

If the atmospheric boiling point and the critical temperature and pressure of a compound are known, a rough estimate of the vapor pressure at intermediate temperatures can be made by plotting these two points on a logarithm of pressure versus the reciprocal of absolute temperature and drawing a straight line between the two points. Heats of vaporization have been estimated by several corresponding states methods. Several equations have been developed to express the dependence of vapor pressure on temperature. One of the most widely used is the Antoine equation.

A semiempirical correlation of boiling point with vapor pressure is provided by the pressure-temperature nomograph. Smoothly-curving empirical correlations of latent heat of vaporization with molecular mass have been reported for series of chloromethanes and chlorofluoromethanes (Reference 29). Correlations of boiling point with molecular mass for series of halogenated methanes and ethanes were also reported.

Strong empirical correlations have been reported among several other properties for limited series of halocarbons, and these correlations can be extended to additional series of compounds. A study of eight physical properties of a series of 25 halogenated hydrocarbons (including alkenes) yielded strong empirical correlations among several properties (Reference 30). The boiling point correlated with heat of vaporization, molar refraction, critical temperature, and surface tension. Heat of vaporization correlated with molecular weight, critical temperature, and surface tension. Molar refraction correlated with molecular weight, critical temperature, and surface tension. For empirical correlations, we examined trends in physical properties in two series of well-studied halocarbons, and in numerous series of halocarbons for which fewer physical properties are known.

SECTION VII

BIOLOGICAL STRUCTURE-ACTIVITY RELATIONSHIPS

A. INTRODUCTION

Over 2000 one-, two-, and three-carbon halogenated hydrocarbons containing combinations of hydrogen, fluorine, chlorine, bromine, and iodine are possible. Toxicological data are known on only a select few of these chemicals. Because of the high costs associated with performing toxicological research, both in terms of dollar amounts and animal lives, the method of predicting certain toxicological parameters for screening the large number of halocarbon chemicals is attractive. Thus, this effort was undertaken to compile the pertinent available information on published methods for predicting toxicological endpoints and to establish guidelines for future work needed to fill in the gaps of estimation techniques.

The view that a relationship exists between the chemical structure and its biological properties is well-established. This relationship was suggested as early as 1848 by Blake who proposed that the biological activity of a salt is due to its basic or acidic component rather than the whole salt (Reference 31). For example, he suggested that the poisonous properties of lead acetate or nitrate were due to the lead and not the acidic components. This was truly remarkable given that the theory of electrolytic dissociation was not put forth until 1884 by Arrhenius. Furthermore, in 1858 the Russian chemist Borodin wrote that, when one compares toxic substances with each other, a relationship exists between the toxicological properties and the chemical constituents.

The formal correlation of biological activity with physicochemical parameters had its roots in the latter part of the nineteenth century with the study of pharmacological action in animals and therapeutic efficacy in humans. By the beginning of the twentieth century, two philosophical approaches to structure-activity relationships emerged. The first school of thought was based on the idea that chemical constituents were the foundation for

understanding biological activity of chemicals. The second focused on the importance of physical properties of chemicals relating to their biological activities. The modern approach to quantitative structure-activity relationships typically stresses both structural features of molecules as well as physical properties to predict biological activities.

It is generally agreed that the use of mathematical models, also known as quantitative structure-activity relationships (QSARs), represents a valuable tool in predicting missing toxicological data. However, the predictive power and range of applicability of a QSAR are strictly dependent upon the chemicals used to define the model. Generally, one criterion for developing a QSAR is that the chemicals in the model must exert biological activity through the same physiological mechanism. Therefore, a crucial point in the formulation of a QSAR is the selection of the data set and its applicability to represent all compounds in a test series. Statistical designs provide appropriate means to optimize the data set selection and render models with good predictive power. Equally important as the data set selection is the realization that a multitude of variables influence the toxicological end-results, for example, animals species, strains, and experimental conditions as well as other factors.

Several toxic endpoints are important to consider when assessing the biological activity of halocarbons. Review of the literature indicates that several commonly noted responses to halocarbons occur. The most important of these are acute lethality, anesthesia, cardiac sensitization, hepatotoxicity, carcinogenicity, and mutagenicity. Acute lethality due to halocarbon exposure is often the result of extreme central nervous system depression leading to respiratory malfunction among other conditions. The mechanism of anesthesia is not completely agreed upon, however, several theories have been put forth ranging from solubilization of the chemical in the lipid bilayer of neuronal material to the chemical formation of minute hydrate crystals of the clathrate type. Hepatotoxicity is a broad term relating to adverse effects on the liver. Since the liver is one of the primary sites for xenobiotic (foreign chemical) metabolism, this organ is particularly susceptible to chemical injury. Carcinogenicity is the production of cancer in the form of tumor due to exposure to a carcinogen. Carcinogens can cause cancer either due to genetic or nongenetic causes.

Nongenetic agents that do not directly interact with the chromosomal material, but which may cause changes in the methylation patterns of the tertiary structure of DNA, are considered epigenetic carcinogens. Genetic carcinogens act through interaction with chromosomal material and are thus considered mutagens as well. Mutagenicity is the alteration of genetic material leading to fertility disorders, embryonic and perinatal death, malformations, hereditary diseases, and cancer. In general, the alterations in the genetic material can be divided into point mutations, which involve a change in a single DNA base pair or chromosomal aberrations such as gaps, breaks, translocations, and changes in chromosome number. Genotoxic carcinogens and mutagens, probably because of their effects on DNA, usually produce tumors in more than one organ, have short latent periods, are occasionally effective after a single exposure, and frequently are carcinogenic in subtoxic doses (Reference 32).

B. STRATEGY FOR FORMULATING A QSAR

Jonsson and co-workers (Reference 33) summarized the strategy for designing QSAR models. According to this well-recognized method, the chemicals must first be divided into classes based on their chemical structure. This differentiation follows the criteria that only chemicals that exert biological action via the same mechanism may be used to produce predictive models. The chemical classes may overlap but must be sufficiently narrow so that the mechanism of biological action is the same for each chemical in the category. Statistical analysis may provide information on outliers to suggest that these chemicals have mechanisms of action different from those of the other chemicals in that class. The second step in the strategy is to develop appropriate ways to describe the physical and chemical differences of each compound in the classes. The objective is to have as few design variables as will adequately describe the chemicals but generally no more variables than two-thirds the number of chemicals as are in the entire data set. The selection of which physicochemical parameters to use is discussed in detail below. The third step in the strategy is to select a set of chemicals on which the model is based. These chemicals should be distributed and well balanced over the entire class of chemicals. High quality biological data

must be available for each of the compounds. The next step in the model building is the statistical analysis. A statistical relationship is devised relating the matrix of physicochemical and structural parameters with the biological data. Multiple regression analyses are often used and occasionally, depending on the sophistication needed, a projection method such as partial least-squares projection to latent structures should be used. After the model is developed, the final step is to apply the QSAR to predict biological activity of compounds where this information is known. This allows a validation of the model and an assessment of its predictive power. The validation compounds should be well distributed over the entire domain of chemicals of interest.

C. SELECTION OF PHYSICOCHEMICAL PARAMETERS

In order to correlate biological activity with molecular structure, the chemical must be adequately described. As with other forms of QSARs, the power of the predictive algorithm is only as good as the data set and chemicals descriptors. As mentioned previously, descriptors are of two types: physical property descriptors and molecular structure descriptors. Selection of physicochemical parameters is made based on knowledge of biological activities of the chemicals in the data set. Structural descriptors are chosen in order to describe sufficiently the molecules being studied. The individual parameters are discussed below.

1. Hydrophobicity (Lipophilicity)

The term "hydrophobic interaction" generally refers to the tendency of the nonpolar portions of molecules or ions to associate in aqueous solutions (Reference 31). Many hydrophobicity parameters have been used as predictors of biological activity. These include partition coefficients, chromatographic coefficients, molar refraction, and parachor. Molar refraction and parachor also take into account steric considerations and will be discussed later. The physicochemical parameter relating lipophilicity most widely used in QSARs is the octanol-water partition coefficient, K_{ow} . This parameter is defined as the

equilibrium ratio of the concentration of the compound in the nonaqueous and aqueous phases, as shown in Equation (20)

$$K_{ow} = C_{octanol}/C_{H_2O}(1 - \alpha) \quad (20)$$

where $C_{octanol}$ and C_{H_2O} are the concentrations in the octanol and aqueous phases, respectively, and α equals the degree of ionization in the aqueous phase. Although many other organic solvents have been used, octanol holds several advantages, one of which is the availability of data on a large variety of chemicals. Also, octanol has a wide range of measurability, and it easily undergoes phase separation with water. In addition, $\log K_{ow}$ is easily estimated, based on molecular substituents.

The U.S. Environmental Protection Agency has derived several QSARs for aquatic toxicity based exclusively on $\log K_{ow}$ data (Reference 15).

2. Polar or Electronic Effects

One of the most widely used electronic parameters for predicting the biological activity of molecules has been the Hammett sigma (σ) constant. For homologous series, the Hammett sigma constant describes the substituent effect on the electron density at a remote site. It is defined by

$$\sigma_X = \log K_{aBX} - \log K_{aBH} \quad (21)$$

where $\log K_{aBH}$ is the logarithm of the acid dissociation constant of parent compound and $\log K_{aBX}$ is the corresponding value for the substituted chemical. Since the original inception, a number of modified Hammett sigma values have been proposed to describe a variety of different chemical reactions.

3. Steric Effects

Steric parameters have been found to be very significant in the prediction of biological activity. In classic linear free-energy QSARs, the steric effects of substituents are considered to retard reactions, in other words, larger substituents reduce the rate or equilibrium constant. Originally, Taft studied the effects of different substituents on the acid hydrolysis of esters of aliphatic acids. He defined a parameter (E_s) to describe steric factors using the following relationship:

$$\delta E_s = \log K_x/K_o \quad (22)$$

where K_x and K_o are the rate constants for hydrolysis of the substituted and unsubstituted ester, respectively, and δ is a constant for the given system being considered. For example, acid hydrolysis of esters, $\delta = 1.00$. For a more comprehensive discussion of the Taft parameters the reader is directed to References 34 and 35. Generally, the Taft parameter is used in reference to chemicals in homologous series and is often used in combination with other parameters relating steric considerations. For example, molar refraction is also used as a steric parameter instead of or in combination with the Taft E_s parameter.

The molar refraction, MR, is defined as

$$MR = [(n^2-1)/(n^2+2)][M/d] \quad (23)$$

where n is the refractive index, M is the molecular weight, d is the density in grams per cm^3 , and (M/d) is the volume occupied by one mole of the compound. The units of MR are cm^3 . To a first approximation, MR is independent of temperature or physical state, and it provides an approximate measure of the actual total volume (without free space) occupied by the molecules in one mole of the substance. The molar refraction is also related to the polarizability α by the Lorenz-Lorentz equation

$$R = 4\pi N\alpha/3 \quad (24)$$

where N is Avogadro's number. For a very large number of compounds MR may be approximated for a molecule by adding the contributions of the constituent atoms shown in Table 13.

TABLE 13. ATOMIC CONTRIBUTIONS TO MOLAR REFRACTION.^a

Atom	Refraction
C(sp ³)	2.418
H	1.100
F	0.81
Cl	5.967
Br	8.865
I	13.900

^aReferences 22 and 36.

For example, the molar refraction of CHClF₂ (HCFC-22) can be calculated as follows:

$$\begin{aligned}
 &1 \text{ carbon} + 1 \text{ hydrogen} + 1 \text{ chlorine} + 2 \text{ fluorine} = \\
 &2.418 + 1.100 + 5.967 + 2(0.81) = 11.11 \text{ cm}^3
 \end{aligned}$$

Similarly, for the slightly more complex molecule CHCl₂CF₃ (HCFC-123)

$$\begin{aligned}
 &2 \text{ carbons} + 1 \text{ hydrogen} + 2 \text{ chlorines} + 3 \text{ fluorines} = \\
 &2(2.418) + 1.100 + 2(5.967) + 3(0.81) = 20.30 \text{ cm}^3
 \end{aligned}$$

Molar refractivity is linearly related to both hydrophobic parameters and van der Waals volume, therefore, care must be used when using molar refractivity in correlations containing these other parameters.

Van der Waals radius (and the corresponding volume) is another way to measure molecular size. The van der Waals radius is the effective radius of a molecule during collision and condensation; molecules are assumed to be spherical.

Recently, Verloop and co-workers (Reference 37) have derived five factors describing steric effects: L , the length of the molecule along its longest axis, and B_1 through B_4 to measure the thickness of a given substituent along its main axis. These parameters offer two main advantages: they describe more adequately the nonsymmetrical substituents and emphasize the vectoral character of steric effects while also providing additional information on the actual conformation of the molecules.

4. Molecular Structure Descriptors

Molecular connectivity has been used extensively in developing QSARs. The usual method is to calculate a number of connectivity indices for each molecule in a data set and then, through multiple linear regression analyses, to find the best equation or equations correlating biological activity with one or more index term(s). Indeed, often the "best" equation is the one that allows ease of calculation based on structural descriptors. For instance, an equation using the sixth-order molecular connectivity term may provide the best fit statistically while an equation using the easily calculated first-order term may be good enough for initial screening purposes.

One of the attractive features of using molecular connectivity indexes as parameters in QSARs is the relative ease in acquiring the necessary descriptors for chemicals in the data set. Knowledge of the chemical structure is the only required information. The aid of a computer program to calculate the molecular connectivity indices is helpful when dealing with a large data set, but such calculations can also be done manually. The details of calculating molecular connectivity indices have been discussed previously.

D. DATA REQUIREMENTS FOR QSAR DEVELOPMENT

The necessary elements for the development of QSAR models are the following: (1) a data set of verified consistent biological data for the endpoints of interest; (2) a set of parameters that describe the chemicals to use in modelling the endpoint; (3) statistical techniques such as multivariate and discriminant analyses for weighting the parameters in near optimum fashion for the explanation of the endpoint; and (4) computer technology to make the modelling practical. It is understood that the biological data must be relevant to the endpoint of interest and that all the data are consistent with each other in terms of species, route and length of exposure. For example, one cannot draw conclusions on lethal concentrations in rats from 90-day oral exposures from data on anesthetic properties in mice from 30-minute inhalation exposures.

The set of parameters that describes the chemicals, which generally relate to physical properties, must be relevant to the endpoint of interest. Accordingly, the use of molecular parameters in the model must have a theoretical basis; e.g., one theory of the mechanism of anesthesia relates to the solubility of agents. Consequently, appropriate physical property parameters would be measures of solubility, lipophilicity, and hydrogen-bonding capability.

The information gained from toxicity modelling is a means of (1) selecting from a larger set of chemical candidates those compounds least likely to have toxic effects and which warrant further investigation, and (2) prioritizing the chemicals of interest in terms of their toxic endpoints. To date, researchers have devised models for predicting acute toxicity, anesthesia, carcinogenicity, mutagenicity, and skin and eye irritation of various chemical classes. For example, extensive work has been performed on modelling the acute toxicity of chlorinated hydrocarbons; however, this work has not been extended to other classes of halogenated hydrocarbons or ethers. Compilations of known methods for predicting anesthetic dose, aquatic toxicity bioconcentration factor, and lethal dose, are provided in Appendix A.

SECTION VIII

RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

A. RESULTS

The results of the 5/8-scale cup-burner tests on 53 halocarbons have been presented in Table 5. Using these data, an improved algorithm for predicting fire-suppression concentrations of haloalkanes has been developed; this formula is given in Equation (4).

Several candidate agents showed excellent extinguishment. On a per-gas-volume (per-mole) basis the most effective extinguishants were Halocarbons 124B1 (2.80 percent), 217I1 (3.15 percent), 217jbI1 (3.04 percent), 7-1-17B1 (2.44 percent), 115I1 (2.09 percent), 123aB1 (3.12 percent), 123aB2 (1.88 percent), 123B2 (2.01 percent), and 5-1-13I1 (3.35 percent). Of these agents, all except the last showed extinguishment superior on a per-gas-volume basis to that of Halon 1211 (3.22 percent).

Physical property prediction methods have been developed and, in some cases, used to determine properties of halocarbons (Appendix A).

B. CONCLUSIONS

Those chemicals showing the best extinguishment are second-generation candidates. Work on manufacturability, environmental assessment, and, most important, toxicity will be required before these and related chemicals can be brought to larger-scale testing. In many cases, laboratory-scale testing will also be needed.

In the short term, first-generation agents—HCFCs, HFCs, and FCs—are required. Since only those with higher boiling points are suitable for extinguishment, only perfluorohexane (FC-5-1-14) and HCFC-123 can be considered for immediate use. A large

number of other first-generation candidates with suitable physical properties exist; however, these are not immediately commercially available.

Extinguishing ability is highest for bromine- and iodine-containing compounds and generally increases with molecular weight.

Physical property estimation methods have been shown to be valuable for screening and prioritization of chemicals, particularly the second-generation candidates for which little data exist.

C. RECOMMENDATIONS

The near-term materials FC-5-1-14 and HCFC-123, either pure or as blends, should be tested at intermediate scale to meet the Air Force mandate for a near-term streaming agent.

The candidate agents listed in Table 14, which are primarily second-generation candidates, should be investigated further. Those candidates predicted to have desirable toxicological, physical, and environmental properties should be assessed further for manufacturability. Once this is done, the top second-generation candidates should be obtained and tested for toxicity and combustion products, two of the characteristics of greatest concern for many of these materials.

The following properties of interest should be predicted for all compounds: boiling point, liquid density, anesthetic dose, lethal concentration.

Additional structures of interest should be added to the NMERI HALOCARBON DATABASE. These should include additional one- to four-carbon bromides and iodides.

TABLE 14. TOP CANDIDATE SECOND-GENERATION STREAMING AGENTS.

Formula	Name	BP (°C)	Est. ODP	CAS No.	Comments
CHBr ₂ F	Dibromofluoromethane	65	0.1	1868-53-7	Undergoes both photolysis and H removal in troposphere.
CHBr ₂ CF ₃	2,2-dibromo-1,1,1-trifluoroethane	73	0.1	354-30-3	Should be excellent extinguishant: large molecule with 2 Br plus CF ₃ . Undergoes both photolysis and H removal in troposphere.
(CF ₃) ₄ C	perfluoroneopentane	---	0	-----	Should be very effective with four pentane CF ₃ groups.
CF ₃ I	trifluoroiodomethane	-23	< 0.1	2314-97-8	Undergoes photolysis in troposphere. Similar extinguishant to CF ₃ Br.
CF ₃ CF ₂ I	iodoperfluoroethane	12	< 0.1	354-64-3	Effective, photolyzed in troposphere.
CF ₃ CF ₂ CF ₂ I	perfluoro- <i>n</i> -propyl iodide	41	< 0.1	754-34-7	Effective, photolyzed in troposphere.
CF ₃ CFICF ₃	perfluoroisopropyl iodide	40	< 0.1	677-69-0	Effective, photolyzed in troposphere.

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APPENDIX A

ESTIMATION METHODS FOR PROPERTIES OF INTEREST

A. ANESTHETIC DOSE

1. Description of the Property

An anesthetic is a chemical that induces loss of sensation in a specific part or all of the body. Compounds that cause loss of sensation in part of the body are local anesthetics; those that affect the whole body are general anesthetics. Common general anesthetics include hydrocarbons, ethers, and miscellaneous other compounds including tribromoethanol, nitrous oxide, and barbiturates. Local anesthetics include alkaloids such as cocaine, synthetic products of the procaine group such as Novocaine and alkyl esters of aromatic acids for topical use, and quinine hydrochloride. Anesthetic dose is the quantity of a compound required to effect anesthesia in a given percentage of cases. For example, AD_{50} is the dosage required to anesthetize 50 percent of an exposed test population.

2. Theoretical Correlations

Davies and co-workers investigated a theoretically-based phase model for estimating the anesthetic potency of halogenated hydrocarbons using a hydrogen bond proton donor scale for a set of 45 closely related chemicals (References A-1 and A-2). The model estimates the anesthetic potential as a function of the dominant intermolecular interactions assuming infinite dilution in a given phase. For this class of halocarbons, the function simplifies to an empirical relationship describing the anesthetic activity in mice in terms of the compound's van der Waals interactions and hydrogen bond donor abilities.

Data on anesthetic potencies of 45 halocarbons were taken from a comprehensive collection of work done by Davies' and other laboratories. Ten mice were enclosed in a test chamber containing air and the anesthetic compound at a constant pressure

of 1 atmosphere. Potency was measured as the concentration by volume percent at which 50 percent of the mice were in the side or prone positions after 30 minutes of exposure to the chemical. This dosage or concentration was termed the AD₅₀ value. The AD₅₀ values are considered to be accurate within 10-15 percent. They were converted to a natural logarithm scale, and the standard error was taken as $\pm 0.14 \log_e$ units.

In the model development, Davies et al. established a scale of acidity for the influence of polar hydrogen in a compound and an estimate of the van der Waals interaction. A scale for halogen influence on acidity was adopted, counting a halogen on a carbon atom attached to the acidic hydrogen as one, while the influence of halogens on each adjacent carbon atom is reduced by a factor of three. The total halogen influence, H_{ai} , on the i th hydrogen is the sum of all the halogen contributions.

The nonpolar or van der Waals interaction contribution, P_o , is based on the following term values:

C - C	0.17	(± 0.02)
C - F	-0.03	(± 0.02)
C - H	0.17	(± 0.02)
C - Cl	0.66	(± 0.04)
C - Br	0.96	(± 0.06)

where the total interaction is a sum of the values for each bond type in the molecule.

A fit of the 45 data points yielded Equation (A-1) ($R^2 = 0.988$, root square deviation = ± 0.20) shown below:

$$\begin{aligned} \log_e AD_{50} = & 5.96 (\pm 0.18) - 2.20 (\pm 0.07) P_o \\ & - \delta_1 [0.64 (\pm 0.05) H_{a1} - 0.43 (\pm 0.10)] \\ & - \delta_2 [0.49 (\pm 0.07) H_{a2} - 0.16 (\pm 0.15)] \end{aligned} \quad (A-1)$$

where $\delta_i = 0$ if $H_{ai} \leq 1.3$ or $\delta_i = 1$ if $H_{ai} > 1.3$.

The model indicates that a fully activated acidic hydrogen increases the anesthetic potency by 1.5 $\log_e$ units. Also, it was determined that the influence of a second acidic hydrogen was not detectably different from a simple additivity relationship.

Further refinement of the equation was done to take into account the steric influences of chlorine and bromine atoms. Therefore, steric influences on an acidic hydrogen of the type -CHXY, where neither X nor Y is a fluorine atom, is introduced by the factor δ_{is} :

$$\log_e AD_{50} = 6.18 - 2.30 P_o - \sum \delta_i \delta_{is} [0.80 H_{ai} - 0.76] \quad (A-2)$$

where $\delta_{is} = 1$ if the hydrogen atom is of the type -CHXY (X or Y = F) or if the group is adjacent to a CF_3 group. Otherwise, $\delta_{is} = 0.75$.

This algorithm provides a good theoretically-based prediction of anesthetic dose in a mouse population; however, the terms are somewhat difficult to calculate, and an effort to automate the algorithm would be extensive.

3. Empirical Correlations

Several models based on empirical correlations of structural features of halocarbons have been used to determine anesthetic dose. Two research groups have specifically studied quantitative models for halocarbons of interest to this program (References A-3 and A-4). The Di Paolo, Kier and Hall study was based on a previous one where the anesthetic potency correlated well with a combination of a molecular connectivity term and an electronic charge description of a diverse group of anesthetic gases. The electron charge term was based on the principle of polar hydrogens influencing potency as used by Davies et al. In order to tailor the QSAR specifically to halocarbon anesthetics, Di Paolo's group

applied the same techniques used in the broader study to the group of 45 halogenated hydrocarbons studied by Davies' group. In this case the polar hydrogen contribution was computed based on derivatives of the Swain and Lupton F values (References A-5 and A-6). The F values are used directly as an index of the polarity of the C - H bonds in the presence of halogen influence. Table A-1 provides the numerical F values.

TABLE A-1. C-H BOND POLARITY INDEXES (F VALUES).

Halogen	Q _H Contribution
F	0.43
Cl	0.41
Br	0.44
I	0.40
α -F	0.13
α -Cl	0.10
α -Br	0.09
β -F	0.05
β -Cl	0.05
β -Br	0.05

The summation of all appropriate F values constitutes the entire C-H bond polarity, Q_H. In the case where no halogen is attached to a C - H fragment, Q_H is taken as zero, except when a methylene group (-CH₂-) is flanked by two halogen-substituted methyl groups as in CF₃CH₂CF₂Cl and CF₃CH₂CF₂Br. In this case, the total Q_H value is obtained by summing both C - H fragments.

The analysis was initially performed investigating molecular connectivity index terms up to the third order. Consistent with what other groups had found, the single index term giving the best correlation against AD_{50} was $^{\circ}\chi^v$ ($r = 0.70$); therefore, this index term was used in the final algorithm along with the polarity index terms, Q_H .

$$\text{Log}_e AD_{50} = 5.229 (\pm 0.171) - 1.026 (\pm 0.044) ^{\circ}\chi^v - 1.054 (\pm 0.053) Q_H \quad (\text{A-3})$$

where $r = 0.975$, and $p < 0.001$. The quantities in parentheses for each regression parameter are the standard deviations calculated in the regression routine. Based on information derived from the QSAR and data set, the authors made several generalizations about relationships of halocarbon anesthetics:

The following conclusions can be drawn from the work to date on prediction of anesthesia:

- (a) Halogenation of hydrocarbons increases the anesthetic potency in the following order: $F < Cl < Br$.
- (b) Fluorination usually decreases potency.
- (c) Dibromides and dichlorides tend to be more potent than their monosubstituted analogs. Dibromides are more potent than corresponding dichlorides.
- (d) Potency increases in homologous series whereby methylene groups are added to the unsubstituted end of the molecule. For example, $CClF_2CH_2CH_3$ is more potent than the corresponding ethane molecule, $CClF_2CH_3$.
- (e) A fully-activated acidic hydrogen atom increases the anesthetic potency by 1.4 $\log_e$ units, and the influence of more than one acid hydrogen can be approximated by a simple additive relationship.

The QSAR developed by Di Paolo and associates (Reference A-3) provides an easy means of predicting anesthetic doses for halocarbons in mice. The parameters are simple to derive, and the equation does take into account that acidic hydrogens contribute to anesthetic activity.

Bindal, Singh, and Gupta attempted to better the well-known correlation between anesthetic dose and boiling point with the addition of molecular connectivity index terms (Reference A-4). They used the first-order connectivity term in combination with boiling points and found that the correlation was no better than simply using boiling point alone. This group considered the molecular connectivity terms in QSARs of limited usefulness.

4. Assessment of Estimation Methods

Two powerful QSARs exist to predict the anesthetic potency of halogenated hydrocarbons. Their usefulness depends on the ease desired in calculating the parameters and the necessity for a complete theoretical basis. On one hand, Davies et al. (References A-1 and A-2) predicted anesthetic activity using predominantly theoretically based parameters; however, the equation, is cumbersome and its use is not obvious. On the other hand, Di Paolo et al. have developed a simple algorithm to calculate the desired variable (Reference A-3), but the equation is only partially based on theory.

The largest body of data in the open literature on anesthetic activity has been generated on mice populations. Most, if not all, QSARs developed specifically for halocarbons use the same data set of 45 halogenated hydrocarbons. Unfortunately, this data set does not completely represent the diversity of chemicals in the halocarbon family. In addition, it is often desirable to compare anesthetic properties of halon replacements in the rat species since modern toxicology frequently uses the rat species as the model for a chemical's activity in humans. Nonetheless, the algorithms previously derived by other researchers provide useful tools in predicting the anesthetic activity of halocarbons in the absence of other QSARs using other animal species and wider range of test compounds.

B. ATMOSPHERIC LIFETIME

1. Description of the Property

Atmospheric lifetime is the time it takes for the quantity of a chemical released to drop to $1/e$ or approximately 37 percent of its initial value, and corresponds to 1.41 half-lives. Potential sinks for halocarbons include photolysis, washing out, and reaction with hydroxyl radical (if H is present). For many hydrogen-containing compounds tropospheric destruction by $\cdot\text{OH}$ is the main sink. Lifetimes for H-containing haloalkanes correlate with the interrelated factors C-H bond strength, activation energy, and rate constant for removal of H by $\cdot\text{OH}$. Washing out in rainfall and dissolution in the oceans or other bodies of water depends on the volatility of a compound, as measured by such interrelated factors as boiling point, vapor pressure, water solubility, and Henry's constant. For the highly volatile, relatively nonpolar halocarbons under consideration in this study, the boiling points are low, vapor pressures are high, water solubilities are low, and Henry's law constants are high. As a result, the quantities of halocarbons removed by this sink are relatively small and can, to a first approximation, be ignored. Photolysis becomes increasingly significant as molecules reach the stratosphere.

Formation of a halogen radical occurs when a haloalkane absorbs a photon having sufficient energy to break the carbon-to-halogen bond, as seen in Reaction [A-1].



This photolysis process is the primary pathway for destruction of haloalkanes in the stratosphere, and occurs to some extent in the troposphere as well. An understanding of the rate of photolysis is important for estimating atmospheric lifetimes of haloalkanes. It is also relevant to the understanding of the rate of generation of chlorine and bromine radicals in the stratosphere, and therefore the ozone-depletion potential. The photolysis rate of a sample is a function of bond strength, intensity and wavelength of light, and absorption cross section.

Rigorous two-dimensional calculations require as input experimentally-determined photolytic cross sections and rates of reaction with hydroxyl radical, require substantial computing time, and cost thousands of dollars per compound. We have developed a simple algorithm that is easy and inexpensive to apply and accurate enough for initial screening purposes. The theoretically supportable algorithm predicts tropospheric lifetimes of one- and two-carbon HFCs and HCFCs within a factor of 2.6 (Reference A-7). Lifetimes can also be calculated for molecules containing two different types of hydrogen atoms. The NMERI algorithm generates estimated tropospheric lifetimes for compounds with atmospheric lifetimes under 30 years.

2. Theoretical Correlations

The tropospheric lifetime (τ) is the inverse of the rate constant for reaction with $\cdot\text{OH}$ (Reference A-8).

$$\tau = 1/k' \quad (\text{A-4})$$

where the pseudo first-order rate constant k' incorporates the average tropospheric $\cdot\text{OH}$ concentration. If two types of hydrogen are present, the total lifetime can be computed using Equation (A-5).

$$1/\tau_{\text{total}} = 1/\tau_1 + 1/\tau_2 \quad (\text{A-5})$$

Activation energy (E_a) for hydrogen atom abstraction can be estimated by Equation (A-6).

$$E_a/R = A + Bn_{\alpha\text{-Cl}} + C_{2C} + Dn_{\beta\text{-F}} + En_{\beta\text{-Cl}} \quad (\text{A-6})$$

where A, B, C, D, and E are constants fitted to the data, and n with the subscripts α or β and F or Cl represents the number of alpha or beta fluorine or chlorine atoms present, respectively. The term C_{2C} indicates a term to be added only if the compound contains two

carbon atoms. This scheme considers, as a first approximation, the contributions of the first, second, and third substituent of each type to be equal. It has the advantage of only requiring five parameters. This equation applies only to one- and two-carbon haloalkanes containing at least one hydrogen atom and no bromine or iodine (only fluorine and/or chlorine). The best fit for compounds with atmospheric lifetimes below 30 years was obtained using $A = 1884$, $B = -438$, $C = -799$, $D = 252$, and $E = 192$, which gave $r^2 = 0.86$ for 16 compounds (11 degrees of freedom).

An equation can be derived from existing formulas for the relationship of activation energy to tropospheric lifetime.

$$\tau = 0.00201(M/n_H)\exp[(E_a/R-450/277)] \quad (A-7)$$

Substituting the equation for E_a/R with numerical parameters into the equation for the lifetime and combining constants gives the equation

$$\tau = 0.356(M/n_H)\exp(-1.581n_{\alpha\text{-Cl}} - 2.884n_{2\text{C}} + 0.910n_{\beta\text{-F}} + 0.693n_{\beta\text{-Cl}}) \quad (A-8)$$

The only two compounds for which the estimated lifetime was not within a factor of 2.6 of the rigorously calculated lifetime were the two longest-lived species, HFCs 23 and 143a. Several factors may enter into this discrepancy. Calculated lifetimes of over 30 years are considered less reliable than shorter lifetimes. For long-lived compounds a larger fraction will reach the stratosphere (passing above most $\cdot\text{OH}$ radicals), and photolysis in the stratosphere will be the main destruction mechanism. The algorithm was therefore fitted using only compounds with lifetimes below 30 years (omitting HFCs 23 and 143a). Estimated tropospheric lifetimes for all one- and two-carbon HFCs and HCFCs calculated from this equation are given in Table A-2, together with the rigorously calculated lifetimes (when available) for comparison.

TABLE A-2. PREDICTED LIFETIMES FOR 1- AND 2-CARBON HFCs, HCFCs.

Halocarbon No.	Formula	Lifetime (yrs)		ODP	
		Rigorously Calculated	Estimated	Rigorously Calculated	Estimated
20	CHCl ₃		0.33		^a
21	CHCl ₂ F	1.9	1.4		0.01
22	CHClF ₂	14.2	5.5	0.05	0.03
23	CHF ₃	^b 411	21		0.00
30	CH ₂ Cl ₂		0.55		^a
31	CH ₂ ClF	1.3	2.1		0.01
32	CH ₂ F ₂	6.7	7.1		0.00
40	CH ₃ Cl		0.94		^a
41	CH ₃ F	3.7	2.6		0.00
120	CHCl ₂ CCl ₃		1.4		0.03
121	CHCl ₂ CCl ₂ F		1.6		0.03
121a	CHClFCCl ₃		6.1		0.11
122	CHCl ₂ CClF ₂		1.8		0.03
122a	CHClFCCl ₂ F		6.9		0.09
122b	CHF ₂ CCl ₃		27		0.12
123	CHCl ₂ CF ₃	1.5	2.0	0.02	0.02
123a	CHClFCClF ₂		7.7		0.06
123b	CHF ₂ CCl ₂ F		30		0.08
124	CHClFCHF ₃	6.0	8.6	0.02	0.03
124a	CHF ₂ CClF ₂		34		0.04
125	CHF ₂ CF ₃	26	37		0.00
130	CHCl ₂ CHCl ₂		0.28		^a
130a	CH ₂ ClCCl ₃		2.8		0.06
131	CHClFCHCl ₂		0.50		^a
131a	CH ₂ ClCCl ₂ F		3.1		0.05
131b	CH ₂ FCCl ₃		12		0.10
132	CHClFCHClF		1.4		0.01
132a	CHF ₂ CHCl ₂		0.66		^a
132b	CH ₂ ClCClF ₂	3.9	3.4		0.04
132c	CH ₂ FCCl ₂ F		13		0.07
133	CH ₂ ClCF ₃	4.5	3.7		0.02
133a	CHClFCHF ₂		2.4		0.01
133b	CH ₂ FCClF ₂		15		0.04
134	CHF ₂ CHF ₂	11.4	6.3		0.00
134a	CH ₂ FCF ₃	14.3	15.6		0.00
140	CH ₂ ClCHCl ₂		0.19		^a
140a	CH ₃ CCl ₃	5.8	7.1	0.14	0.09
141	CHClFCH ₂ Cl		0.53		^a
141a	CH ₂ FCHCl ₂		0.23		^a
141b	CH ₃ CCl ₂ F	7.0	7.7	0.10	0.06
142	CH ₂ ClCHF ₂		0.96		^a
142a	CHClFCH ₂ F		0.85		^a
142b	CH ₃ CClF ₂	17.8	8.2	0.05	0.03
143	CH ₂ FCHF ₂	3.5	2.2		0.02
143a	CH ₃ CF ₃	^b 40	8.6		0.00
150	CH ₂ ClCH ₂ Cl		0.20		^a
150a	CH ₃ CHCl ₂		0.08		^a
151	CH ₂ ClCH ₂ F		0.33		^a
151a	CH ₃ CHClF		0.30		^a
152	CH ₂ FCH ₂ F	0.60	0.82		0.00
152a	CH ₃ CHF ₂	1.56	0.88		0.00
160	CH ₃ CH ₂ Cl		0.11		^a
161	CH ₃ CH ₂ F	0.28	0.30		0.00

^aNonzero but less than 0.01.^bLong-lived species not estimated accurately by algorithm.

For the haloalkanes that each contain two types of reactive hydrogens, lifetimes were computed by calculating a lifetime based on each type of hydrogen separately, then combining the two lifetimes into an overall lifetime according to Equation (A-5). The fact that the estimated overall lifetimes for these compounds are within a factor of 2.2 of the experimental lifetimes supports the validity of the algorithm.

The presence of fluorine on the alpha carbon did not significantly affect the lifetime, and therefore a factor for alpha fluorine atoms was left out of the algorithm. The presence of α -chlorine(s) and of a second carbon atom contribute to lower activation energy and decreased tropospheric lifetime. The presence of fluorine or, to a lesser extent, chlorine in the β position increases activation energy and lifetime. For example, it is predicted that HCFC-123 will have a significantly shorter tropospheric lifetime than its isomer HCFC-123a.

The algorithm for tropospheric lifetime suggests that the following species may be long-lived: 122b, 123b, 124a, 131b, 132c, and 133b. This parameterization scheme can suggest which isomer among several will have a shorter tropospheric lifetime.

C. BIOCONCENTRATION FACTOR

1. Description of the Property

The bioconcentration factor (BCF) is a measure of the potential for residue bioaccumulation in the food chain. It is a proportionality factor relating residue concentration in aquatic organisms to the water concentration when a steady-state condition exists. This factor relies on the concept that residues in fish are a direct function of the chemical in water over a wide range of concentrations. Because a bioconcentration test costs upwards of \$10,000 for each chemical, it is essential that there be a firm technical basis indicating that a chemical has a potential to bioaccumulate. Therefore, it is prudent to estimate the BCF in order to screen for chemicals that are likely to bioconcentrate and test only those showing this possibility.

2. Theoretical Correlations

The US Environmental Protection Agency has adopted the use of a QSAR developed by Veith and Kosian (Reference A-9) relating 28-day fathead minnow BCF to $\log K_{ow}$:

$$\log BCF = 0.79 \log K_{ow} - 0.40 \quad (A-9)$$

where the data set used was 122 chemicals, and the coefficient of determination (R^2) equals 0.927. The QSAR was developed using representative chemicals from the following classes: aromatic amines, cyclodienes, ethers, halogenated alkyls, halogenated aromatics, halogenated indoles, halogenated phenols, and phosphate esters. This QSAR applies to neutral organic chemicals with $\log K_{ow}$ values less than 8.0. For chemicals with higher $\log K_{ow}$ values, an exposure of greater than 28 days would be required for residues to reach equilibrium. Unless a chemical has significant biological activity, it is unlikely that chemicals with $\log K_{ow}$ values less than 4.0 would bioaccumulate to hazardous levels in the human food chain (Reference A-10).

Very few halocarbons were used to develop the QSAR, and those that were used were predominantly the chlorinated hydrocarbons (carbon tetrachloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, hexachloroethane, and hexachlorocyclohexane). Therefore, it is anticipated that the predictive power for other halocarbons may not be very strong.

D. BOILING POINT, HEAT OF VAPORIZATION, AND VAPOR PRESSURE

1. Descriptions of the Properties

The boiling point, heat of vaporization, and vapor pressure at a given temperature for a particular compound are intimately related phenomena. The boiling point of a compound is the temperature at which the molecules have high enough kinetic energy to break the intermolecular attractive forces and create a vapor pressure sufficient to push back

the molecules in the atmosphere above the liquid. At sea level, boiling occurs at a vapor pressure of 760 torr (1 atm); at higher altitudes, boiling occurs at lower vapor pressure (and correspondingly lower temperature). The heat of vaporization is the heat required to disrupt the intermolecular forces and form the vapor at the boiling point. Heat of vaporization is measured in calories or joules per gram or mole. The vapor pressure of a substance is the pressure present above a sample of the liquid when the vapor of that liquid is in equilibrium with the liquid at a specific temperature. It can also refer to the upward pressure of evaporating molecules at a given temperature. When the vapor pressure equals the external (or atmospheric) pressure, the liquid boils. The higher the temperature of the liquid, the higher the vapor pressure.

2. Theoretical Correlations

Three properties associated with phase change between liquid and gas (boiling point, heat of vaporization, and vapor pressure at a given temperature) are closely related for a given compound. A simple relationship, Trouton's rule, exists between the heat of vaporization and boiling point: $\Delta H_{\text{vap}}/T = \text{a constant}$. For one- and two-carbon haloalkanes, we have determined an average value of 86.4 J/mol-K for Trouton's rule, with a standard deviation of 1.4 percent. This rule is followed fairly well by nonpolar liquids and relies on the assumption that the entropy of vaporization is approximately the same for all such liquids. If the heat of vaporization of a compound is considered constant, an extremely useful theoretical equation (the Clausius-Clapeyron equation) can be derived relating the boiling point, heat of vaporization, and vapor pressure. Trouton's rule and the Clausius-Clapeyron equation used together can give all three of the liquid/gas phase-change properties from either the boiling point or the heat of vaporization. Vapor pressure has been estimated using several corresponding states methods including those of Pitzer, Halm-Stiel, Riedel, and Gomez-Nieto-Thodos.

An algorithm has been developed for estimating boiling points based on chemical structures. Boiling points have been estimated by the formula

$$B = (C_1 R^{1.47} + C_2) / P \quad (\text{A-10})$$

where B is the boiling point in kelvins, R is the molar refraction, P is the parachor, and C_1 and C_2 are constants to be fitted. Molar refraction and parachor are based on the molecular structure and can be calculated easily by group additivity. When Equation (A-10) was fitted to the compounds with boiling points reported in the NMERI HALOCARBON DATABASE, it was found that a fair correlation could be obtained for noniodinated compounds using the equation

$$B = (613R^{1.47} + 10360)/P \quad (\text{A-11})$$

with $R^2 = 0.95$ for 321 degrees of freedom and a standard deviation of about ± 30 °C. Equation (A-10) did not fit well for iodinated compounds. Because of the high standard deviation and lack of ability to fit iodinated compounds, another functional form was fitted:

$$B = C_1 R^{C_2} / P^{C_3} \quad (\text{A-12})$$

where C_1 , C_2 , and C_3 are constants.

A robust multiple linear regression for the 350 reported boiling points (including those for iodinated compounds) in the database yielded the equation

$$\ln B = 0.86682 \ln R - 0.42652 \ln P + 5.3723 \quad (\text{A-13})$$

or

$$B = 215.36 R^{0.86682} / P^{0.42652} \quad (\text{A-14})$$

where B is the boiling point in kelvins, R is the molar refraction, and P is the parachor. The quality of fit was $r^2 = 0.939$ for 348 degrees of freedom. The standard deviation in the estimates was ± 15 °C. Boiling points for all compounds in the NMERI HALOCARBON DATABASE were estimated using Equation (A-14).

If the natural logarithm of the vapor pressure of a compound is plotted against $1/T$, where T is the absolute temperature, the slope of that curve at any point multiplied by $-R$ (the negative of the gas law constant) is the heat of vaporization at that temperature.

$$d(\ln P)/d(1/T) = -\Delta H_{\text{vap}}/R \quad (\text{A-15})$$

where P is pressure and ΔH_{vap} is the latent heat of vaporization.

Since the heat of vaporization is fairly constant over short temperature ranges in many cases the curve is a straight line. The latent heat of vaporization varies considerably with temperature. It must decrease with increasing temperature and approach zero at the critical point.

If the heat of vaporization is considered constant, integration of Equation (A-15) gives an extremely useful theoretical equation relating the boiling point, heat of vaporization, and vapor pressure called the Clausius-Clapeyron equation (Equation (A-16)).

$$\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2) \quad (\text{A-16})$$

where P_1 and P_2 are the vapor pressures exerted by the compound at absolute temperatures T_1 and T_2 respectively, ΔH_{vap} is the heat of vaporization expressed as a positive quantity, and R is the gas constant in the appropriate units to correspond with the units of ΔH_{vap} . The boiling point can be taken as one of the temperatures, with a corresponding pressure of 760 torr. Equation (A-16) can be used in several ways. If the boiling point and the vapor pressure at another temperature are known, the heat of vaporization can be calculated. A rearrangement of Equation (A-16) to solve for heat of vaporization is given in Equation (A-17).

$$\Delta H_{\text{vap}} = R \ln(P_1/P_2)/(1/T_1 - 1/T_2) \quad (\text{A-17})$$

Similarly, solving Equation (A-15) for a vapor pressure P_2 yields

$$P_2 = P_1 \exp[(\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2)] \quad (\text{A-18})$$

3. Empirical Correlations

A simple relationship exists between the heat of vaporization and boiling point. This approximation, known as Trouton's rule, states that

$$\Delta H_{\text{vap}}/T_b \approx 22 \text{ cal/mole-degree} = 92 \text{ J/mole-K} \quad (\text{A-19})$$

The constant in Equation (A-19) varies slightly with chemical class. For small haloalkanes, we have found that the appropriate constant in Equation (A-19) is 86.4 J/mol-K instead of 92. This rule is followed fairly well by nonpolar liquids and relies on the assumption that the entropy of vaporization is approximately the same for all such liquids. Trouton's rule arises because, at the boiling point, the chemical potentials in the two phases are identical:

$$\mu_{\text{gas}} = \mu_{\text{liquid}} \quad (\text{A-20})$$

That is,

$$\Delta G^\circ_{\text{gas}} = \Delta G^\circ_{\text{liquid}} \quad (\text{A-21})$$

so

$$\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}} \quad (\text{A-22})$$

or

$$\Delta S^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}}/T \quad (\text{A-23})$$

Table A-3 lists selected haloalkanes with their heats of vaporization, boiling points, and ratios of the two (Reference A-11).

For the group of haloalkanes in Table A-3, the average value ($\pm$ standard deviation) of $\Delta S_v(T_b)$ is $86.4 \pm 1.3 \text{ J/mol-K}$; therefore, this constant is the most appropriate one to use for predictive purposes for haloalkanes. For this group of compounds, the lowest

value is 84.0 (2.7 percent below the average) and the highest value is 88.6 (2.6 percent above the average). The standard deviation of these values from the average is 1.5 percent ($\pm 1.3/86.4$).

More accurate estimates of the heat of vaporization than those obtained from Trouton's rule can be made using knowledge of the vapor pressure-temperature relationship for the compound. Several correlations have been proposed (Reference A-12, p. 249). One equation is derived from the Antoine vapor pressure equation.

$$\Delta H_v = (8.32BT^2\Delta z)/(T + C)^2 \quad (\text{A-24})$$

where B and C are the coefficients in the Antoine equation and Δz is $z_{\text{gas}} - z_{\text{liquid}}$, where z is the compressibility constant, calculated from the equation

$$\Delta z = [1 - (P_r/T_r^3)]^{0.5} \quad (\text{A-25})$$

where P_r is the reduced pressure and T_r is the reduced temperature.

If the atmospheric boiling point and the critical temperature and pressure or boiling point of a compound at two pressures are known, an estimate of the vapor pressure at intermediate temperatures can be made from the Clausius-Clapeyron equation. Furthermore, heats of vaporization have been estimated by several corresponding states methods. Several equations have been developed to express the dependence of vapor pressure on temperature. One of the most widely used is the Antoine equation

$$\ln P = A - B/(T + C) \quad (\text{A-26})$$

where P is the vapor pressure in Torr, A, B, and C are the Antoine coefficients, and T is the absolute temperature in kelvins.

Special care must be taken when using literature-derived Antoine coefficients because the equation appears in many different forms. For example, logarithms may be

TABLE A-3. EXPERIMENTAL PARAMETERS FOR SELECTED HALOCARBONS.

Formula	Name	$\Delta H_{\text{vap}}(25\text{ }^{\circ}\text{C})$ (kJ/mole)	T_b (Kelvins)	$\Delta S_v(T_b)$ (J/mole-K)
CH_3Cl	chloromethane	19.06	248.9	86.2
CH_2Cl_2	dichloromethane	28.56	312.9	88.6
CHCl_3	chloroform	30.81	334.9	85.5
CCl_4	carbon tetrachloride	33.14	349.7	85.7
CHCl_2CH_3	1,1-dichloroethane	30.47	330.4	86.4
$\text{ClCH}_2\text{CH}_2\text{Cl}$	1,2-dichloroethane	34.25	356.6	85.8
$\text{CHCl}_2\text{CH}_2\text{Cl}$	1,1,2-trichloroethane	39.30	386.9	86.1
CCl_3CH_3	1,1,1-trichloroethane	32.74	347.3	85.6
$\text{CCl}_3\text{CH}_2\text{Cl}$	1,1,1,2-tetrachloroethane	42.18	403.7	86.2
$\text{CHCl}_2\text{CHCl}_2$	1,1,2,2-tetrachloroethane	44.99	419.4	86.3
CH_2F_2	difluoromethane	15.11	221.6	84.0
CH_2BrCl	bromochloromethane	32.85	341.3	87.9
CH_2Br_2	dibromomethane	37.37	370.1	88.2

either natural (base e) or base 10, the temperature may be in $^{\circ}\text{C}$ instead of kelvins, and the minus sign on the constant B shown in Equation (A-26) may be included in the constant, in which case the equation should be written with a plus sign before the B.

Smoothly-curving empirical correlations of latent heat of vaporization with molecular mass have been reported for series of chloromethanes and chlorofluoro-methanes. For the series CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 the correlating third-degree polynomial has been found to be

$$\Delta H_v = -0.37556 + (0.163174)M - (1.20350 \times 10^{-3})M^2 + (2.99859 \times 10^{-2})M^3 \quad (\text{A-27})$$

The similar polynomial for the chlorofluoromethane series CF_4 , CF_3Cl , CF_2Cl_2 , CFCl_3 , CCl_4 has been found to be

$$\Delta H_v = 3.97 - (8.81 \times 10^{-2})M + (1.06 \times 10^{-3})M^2 - (2.27 \times 10^{-6})M^3 \quad (\text{A-28})$$

where the heat of vaporization is expressed in kcal/mole, and the correlating polynomials give errors of less than 1 percent for every point.

Correlations of boiling point with molecular mass for series of halogenated methanes and ethanes have also been reported. For bromofluoromethanes (CF_4 to CBr_4)

$$\begin{aligned} \text{BP } (^\circ\text{C}) = & -204.313 + 0.60814 M + 3.15039 \\ & \times 10^{-3} M^2 - 4.24005 \times 10^{-6} M^3 \end{aligned} \quad (\text{A-29})$$

For chloromethanes (CH_4 to CCl_4),

$$\text{BP} = -261 + 6.98 M - 5.20 \times 10^{-2} M^2 + 1.36 \times 10^{-4} M^3 \quad (\text{A-30})$$

For chlorofluoromethanes (CF_4 to CCl_4),

$$\text{BP} = -407 + 3.14 M \quad (\text{A-31})$$

For fluorinating the second carbon of 1-chloro-1-fluoroethane (1-chloro-1-fluoroethane to 1-chloro-1,2,2,2-tetrafluoroethane),

$$\text{BP} = 61.5 + 0.505 M - 7.49 \times 10^{-3} M^2 \quad (\text{A-32})$$

All of these polynomials give average errors of 0.5 °C or less, and the maximum error in the estimated boiling point is 2.1 °C (for CF_4 using the monomial equation).

4. Temperature Dependence

If a value of the latent heat of vaporization at the boiling point is known, the Watson equation can be used to estimate the latent heat at other temperatures (Reference A-12, p. 252).

$$\Delta H_v = \Delta H_{v,b}[(T_c - T)/(T_c - T_b)]^{0.38} \quad (\text{A-33})$$

where ΔH_v is the latent heat of vaporization at temperature T , $\Delta H_{v,b}$ is the latent heat of vaporization at the boiling point, T_b is the boiling point in K, T_c is the critical temperature in K, and T is the temperature in K. Over a limited range of temperature of up to about 100 °C, the variation of latent heat of vaporization with temperature can usually be considered linear.

E. BOND STRENGTHS

1. Description of the Property

Bond strength, also known as bond dissociation energy or enthalpy, is the energy required to break a particular bond.



Note that this is also the negative value of the enthalpy released when two radicals combine to form a new bond.



Bond strength is typically reported in kcal/mole or kJ/mole. The values depend on several interrelated factors including the electronegativities of the atoms involved and substituent and steric effects.

Table A-4 shows the ranges for strengths of various types of bonds interatomic forces (Reference A-13).

TABLE A-4. RANGES OF INTERATOMIC FORCES.

Type	Energy (kJ/mol)
covalent bonds	170-460
ionic bonds	20-40
ion-dipole interactions	4-17
dipole-dipole interactions	4-17
hydrogen bonds	4-17
charge transfer complexes	4-7
hydrophobic interactions	4
van der Waals interactions	2-4

Normal ranges for strengths of various types of covalent bonds are shown in Table A-5 (Reference A-14).

TABLE A-5. BOND STRENGTHS FOR COVALENT BONDS TO SP³ CARBON.

Bond type	Bond Strength	
	kJ/mol	kcal/mol
C-H	385-445	92-107
C-F	440-490	106-117
C-Cl	295-360	71-86
C-Br	270-300	65-72
C-I	200-240	48-58
C-C	270-450	65-107

The bond strength or bond dissociation energy (BDE) is the heat of reaction for a process such as



The bond dissociation energy is then defined by

$$\text{BDE} = \Delta H_{\text{rxn}} = \Delta H_f^\circ{}_{298}(\text{CF}_3) + \Delta H_f^\circ{}_{298}(\text{Br}) - \Delta H_f^\circ{}_{298}(\text{CF}_3\text{Br}) \quad (\text{A-34})$$

In this example, the numerical value of the $\text{CF}_3\text{-Br}$ BDE is $71.7 \text{ kcal mol}^{-1} = 299.7 \text{ kJ mol}^{-1}$. For stable molecules the BDE values will be positive.

2. Previous Estimation Methods Used

Rough estimates (Method 1) of the C-H bond strengths in halocarbons can be made using the equation

$$D_{298} = 91 + \Sigma e_i \quad (\text{A-35})$$

where D_{298} is the bond dissociation energy at 298K in kcal/mole and the e_i column lists the group additivity contributions (Table A-6).

TABLE A-6. GROUP ADDITIVITIES FOR C-H BOND STRENGTHS.

Substituent on Carbon	e_i
H	4.0
F	5.0
Cl	1.6
Br	3.0
I	4.0
CCl_3	2.0
CX_3 (X = Br,I)	0.0
CF_3	5.0
CF_2Cl	5.0
CFCl_2	2.5

A second simple additivity scheme for bond strengths can be devised. The compounds of greatest interest are those containing one or two hydrogens plus some combination of F, Cl, and Br. For one-carbon compounds containing one hydrogen, the combinations of halogens shown in Table A-7 are possible. An examination of the experimental bond strengths for these compounds suggests that the exchange of chlorine and bromine has virtually no effect on the C-H bond strength. A compound of formula CHX_3 , where the three halogens are any combination of Cl and Br including Cl_3 and Br_3 , is estimated to have a C-H bond strength of 96 kcal/mole. Substitution of F for Cl or Br adds 7.7 kcal/mole for the first substitution, 0.5 kcal/mole for the second, and 2.0 kcal/mole for the third. Use of these simple rules gives the estimated (Method 2) bond strengths shown in Table A-7.

It is evident from Table A-7 that Method 2 gives a better correlation with experimental results than does Method 1, which uses the additivity method discussed earlier.

TABLE A-7. C-H BOND STRENGTH ESTIMATES FOR TRIHALOMETHANES.

Substituents	Experimental Bond Strength (kcal/mol)	Estimated C-H Bond Strength (kcal/mol)	
		Method 2	Method 1
F F F	106	106	106
F F Cl	104	104	102.6
F Cl Cl	103.5	98.2	99.2
Cl Cl Cl	95.8	96	95.8
F F Br	--	104	104
F Br Br	103.7	103.7	102
Br Br Br	96	96	100
Cl Cl Br	--	96	97.2
Cl Br Br	--	96	98.6
F Cl Br	--	103.7	100.6

3. Calculation Method

Hess's law states that the enthalpy (BDE) change of a reaction is the same whether the reaction occurs in one step or several steps. Therefore, it is possible to imagine a series of steps leading to the formation of each compound, involving a combination of radicals (see section on Heats of Formation and Reaction). These steps and the values of heats of formation calculated by the AM1 program were used to calculate the BDE values for all of the unique bonds in the family of halomethanes (one-carbon halogenated hydrocarbons). The results are collected in Table A-8.

The required information consists of heats of formation of reactants and products. Heats of formation of one-carbon halogenated hydrocarbons are listed in Table A-9. Heats of formation of the atoms (H, F, Cl, Br, I) were taken from tabulations (Reference A-15). Free radical heats of formation were calculated with the AM1 parameterization in the MOPAC programs as discussed under the section on heats of formation. Dewar et al. have demonstrated that for small hydrocarbon radicals, AM1 heats of formation are virtually as reliable as heats of formation of the parent compounds (Reference A-16). Values for the one-carbon free radicals of halocarbons are reported in Table A-9. It was found in a comparison with 11 reported literature values (given in parentheses) for $\Delta H_f^\circ_{298}$ of the halogenated free radicals that AM1 results are consistently too low by 20.6 ± 7.1 kcal mol⁻¹. The values are off by this amount because the calculation contains an arbitrary constant (starting point, zero point); it is standard practice to reset the baseline for these calculations. Also reported are the adjusted values obtained by adding 20.6 kcal mol⁻¹ to the calculated AM1 results.

4. Reliability

As a result of the uncertainty in the heats of formation of the free radicals, the BDE values are reliable to ± 10 kcal mol⁻¹. A comparison with tabulated BDEs (Reference A-17) shows that the absolute values in Table A-8 are reasonably close (average mean difference is 6.6 kcal mol⁻¹), and that trends are faithfully reproduced. These reproducible

TABLE A-8. BOND DISSOCIATION ENERGIES FROM HEATS OF FORMATION
CALCULATED WITH THE AM1 PARAMETERIZATION.^a

Molecule	(C-H)		(C-F)		(C-Cl)		(C-Br)		(C-I)	
CH ₃ F	101.3	(100.0)	111.2	(109.9)	-	-	-	-	-	-
CH ₂ F ₂	98.0	(101.0)	123.2	(119.0)	-	-	-	-	-	-
CHF ₃	101.1	(106.7)	121.2	(126.0)	-	-	-	-	-	-
CF ₄	-	-	121.2	(130.5)	-	-	-	-	-	-
CH ₃ Cl	109.4	(100.9)	-	-	82.9	(84.6)	-	-	-	-
CH ₂ Cl ₂	100.3	(99.0)	-	-	89.6	(80.1)	-	-	-	-
CHCl ₃	105.1	(85.8)	-	-	80.3	(77.6)	-	-	-	-
CCl ₄	-	-	-	-	81.2	(73.1)	-	-	-	-
CH ₃ Br	106.6	(102.0)	-	-	-	-	64.3	(70.9)	-	-
CH ₂ Br ₂	99.1	(103.7)	-	-	-	-	76.1	-	-	-
CHBr ₃	92.0	(96.0)	-	-	-	-	66.7	-	-	-
CBr ₄	-	-	-	-	-	-	57.1	(56.2)	-	-
CClF ₃	-	-	122.8	(123.0)	68.2	(86.2)	-	-	-	-
CCl ₂ F ₂	-	-	105.2	(110.0)	67.2	(76)	-	-	-	-
CCl ₃ F	-	-	103.8	(101.9)	69.2	(73)	-	-	-	-
CBrF ₃	-	-	110.0	-	-	-	47.9	-	-	-
CBr ₂ F ₂	-	-	99.0	-	-	-	47.0	-	-	-
CBr ₃ F	-	-	83.1	-	-	-	50.7	-	-	-
CBrCl ₃	-	-	-	-	69.9	-	56.0	(55.3)	-	-
CBr ₂ Cl ₂	-	-	-	-	68.7	-	55.7	-	-	-
CBr ₃ Cl	-	-	-	-	67.7	-	56.2	-	-	-
CH ₂ ClF	99.1	-	119.0	-	82.5	(85.3)	-	-	-	-
CH ₂ BrF	98.0	-	117.0	-	-	-	64.8	-	-	-
CH ₂ BrCl	99.7	-	-	-	89.8	-	74.1	-	-	-
CHClF ₂	97.5	(101.6)	114.8	-	73.0	-	-	-	-	-
CHCl ₂ F	96.6	-	106.4	-	75.9	-	-	-	-	-
CHBrF ₂	95.4	-	111.8	-	-	-	53.4	(69.0)	-	-
CHBr ₂ F	93.2	-	108.2	-	-	-	58.0	-	-	-

^aValues in parentheses are experimental results.

TABLE A-8. BOND DISSOCIATION ENERGIES FROM HEATS OF FORMATION
CALCULATED WITH THE AM1 PARAMETERIZATION
(CONTINUED).^a

Molecule	(C-H)	(C-F)	(C-Cl)	(C-Br)	(C-I)
CHBr ₂ Cl	92.7	-	-	79.0	65.4
CHBrCl ₂	93.9	-	-	79.5	64.6
CHBrClF	94.8	144.2	-	74.6	57.9
CBr ₂ ClF	-	86.8	-	65.9	51.0
CBrCl ₂ F	-	90.4	-	67.5	51.3
CBrClF ₂	-	102.1	-	65.5	47.9 (64.5)
CH ₃ I	97.1	-	-	-	82.4
CH ₂ I ₂	104.1	-	-	-	66.6
CHI ₃	148.3	-	-	-	61.2
Cl ₄	-	-	-	-	105.0
CF ₃ I	-	108.9	-	-	34.7
CF ₂ I ₂	-	99.4	-	-	34.1
CFI ₃	-	139.2	-	-	19.3 (55.0)
CCl ₃ I	-	-	102.5	-	42.7
CCl ₂ I ₂	-	-	71.3	-	67.8
CClI ₃	-	-	124.1	-	48.7
CBr ₃ I	-	-	-	59.3	45.9
CBr ₂ I ₂	-	-	-	62.2	48.4
CBrI ₃	-	-	-	115.8	51.5
CHF ₂ I	93.7	111.7	-	-	39.5
CHF ₂ I ₂	93.6	104.6	-	-	46.3
CHCl ₂ I	126.2	-	80.7	-	51.1
CHClI ₂	113.3	121.6	-	-	93.1
CHBr ₂ I	93.4	-	-	69.3	54.7
CHBrI ₂	95.4	-	-	72.6	57.6
CH ₂ FI	98.1	118.9	-	-	44.2
CH ₂ CI	100.9	-	91.9	-	60.3

^aValues in parentheses are experimental results.

TABLE A-8. BOND DISSOCIATION ENERGIES FROM HEATS OF FORMATION
CALCULATED WITH THE AM1 PARAMETERIZATION
(CONCLUDED).^a

Molecule	(C-H)	(C-F)	(C-Cl)	(C-Br)	(C-I)
CH ₂ BrI	101.4	-	-	77.9	63.3
CHClFI	93.7	104.5	74.4	-	44.3
CHBrFI	92.9	102.2	-	58.9	45.2
CHBrClI	93.6	-	80.9	67.4	52.7
CCl ₂ FI	-	123.0	66.8	-	38.1
CClF ₂ I	-	101.4	64.4	-	34.7
Cl ₄	-	-	-	-	105.0
CClFI ₂	-	89.2	66.5	-	38.2
CBr ₂ FI	-	84.5	-	51.2	38.7
CBrF ₂ I	-	98.7	-	46.7	34.6
CBrFI ₂	-	86.5	-	52.7	39.4
CBrCl ₂ I	-	-	69.7	89.0	43.2
CBr ₂ ClI	-	-	69.3	57.9	44.3

^aValues in parentheses are experimental results.

trends are expected to extend to molecules for which experimental values are not available, i.e., a majority of the values in Table A-8.

F. CRITICAL PROPERTIES

1. Descriptions of the Properties

The critical point is the thermodynamic state in which liquid and gas phases of a substance coexist in equilibrium at the highest possible temperature. At this point, a significant change occurs in the properties of a substance. At higher temperatures than

TABLE A-9. HEATS OF FORMATION OF ONE-CARBON FREE RADICALS
OF HALOGENATED HYDROCARBONS AT 298K.

Radical	Calc. ΔH_f° (kcal mol ⁻¹)		Adjusted ^a ΔH_f° (kcal mol ⁻¹)
CH ₃	31.4	^b (35.1)	35.1
CH ₂ F	- 31.1	^b (-7.8)	- 10.486
CHF ₂	- 89.5	^b (-59.2)	- 68.898
CF ₃	-142.8	^b (-111.7)	-122.167
CH ₂ Cl	15.5	^b (28.3)	36.069
CHCl ₂	3.00	^b (24.1)	23.594
CCl ₃	- 4.7	^b (19.0)	15.875
CH ₂ Br	28.9	^b (41.5)	49.548
CHBr ₂	27.0	^b (54.3)	47.636
CBr ₃	26.9	--	47.523
CClF ₂	- 88.1	^b (-64.3)	- 67.543
CCl ₂ F	- 40.0	^b (-23.0)	- 19.408
CBrF ₂	- 72.8	--	- 52.212
CBr ₂ F	- 13.3	--	7.263
CBrCl ₂	7.0	--	27.558
CBr ₂ Cl	17.6	--	38.216
CHClF	- 37.6	^b (-25.0)	- 17.029
CHBrF	- 23.2	--	- 2.605
CHBrCl	15.7	--	36.270
CHBrF	- 23.2	--	- 2.602
CHBrCl	56.5	--	77.142
CBrClF	- 26.0	--	- 5.431

^aAdjusted by adding 20.6 kcal mol⁻¹ to the calculated values.

^bValues in parentheses are from the literature.

TABLE A-9. HEATS OF FORMATION OF ONE-CARBON FREE RADICALS OF
HALOGENATED HYDROCARBONS AT 298K (CONCLUDED).

Radical	Calc. ΔH_f° (kcal mol ⁻¹)		Adjusted ^a ΔH_f° (kcal mol ⁻¹)
CH ₂ I	43.3	--	63.874
CHI ₂	54.2	--	74.819
Cl ₃	114.7	--	135.288
CF ₂ I	- 61.9	--	- 41.295
CFI ₂	10.0	--	30.607
CCl ₂ I	51.6	--	72.165
CClI ₂	42.8	--	63.413
CBr ₂ I	39.1	--	59.697
CBrI ₂	51.6	--	72.239
CHFI	- 10.7	--	9.897
CHCI	29.2	--	49.791
CHBrI	40.4	--	61.023
CHClF	- 37.6	--	- 17.029
CCIFI	- 14.8	--	5.802
CBrFI	- 2.0	--	18.559
CBrCI	30.0	--	50.595

^aAdjusted by adding 20.6 kcal mol⁻¹ to the calculated values.

^bValues in parentheses are from the literature.

the critical temperature no liquid phase can exist. Values for the critical temperatures, pressures, and volumes are needed for prediction methods that correlate physical properties with reduced temperature, pressure, or volume. A reduced temperature, pressure, or volume is the normal value divided by the critical value.

$$T_r = T/T_c \quad (\text{A-36})$$

$$P_r = P/P_c \quad (\text{A-37})$$

$$V_r = V/V_c \quad (\text{A-38})$$

2. Values for Critical Constants

Experimental values for critical constants are found in several sources. Critical reviews of the literature on critical constants for organic compounds, plus summaries of selected values, have been published. If reliable experimental values are unavailable, the critical constants can be estimated with sufficient accuracy for most purposes. For organic compounds Lydersen's method is most often used. This method uses the equations

$$T_c = T_b/[0.567 + \Sigma\Delta T - (\Sigma\Delta T)^2] \quad (\text{A-39})$$

$$P = M/(0.34 + \Sigma\Delta P)^2 \quad (\text{A-40})$$

$$V = 0.04 + \Sigma\Delta V \quad (\text{A-41})$$

where T_c is the critical temperature in kelvins, P_c is the critical pressure in atmospheres, V_c is the molar volume at the critical conditions in m^3/mol , T_b is the normal boiling point, M is the molecular weight, ΔT is the critical temperature increment, and ΔP is the critical pressure increment. ΔT , ΔP , and ΔV are obtained from Table A-10.

TABLE A-10. CRITICAL CONSTANT INCREMENTS.^a

Group	ΔT	ΔP	ΔV
-CH ₃	0.020	0.227	0.055
-CH ₂ -	0.020	0.227	0.055
-CH-	0.012	0.227	0.055
>C<	0.00	0.210	0.041
-F	0.018	0.224	0.018
-Cl	0.017	0.320	0.049
-Br	0.010	0.50	0.070
-I ^b	0.012	0.83	0.095

^aNumbers valid for acyclic compounds only.

^bNumbers based on too few data points to be highly reliable.

G. DIPOLE MOMENT

1. Description of the Property

In many molecules the atomic nuclei and the electrons are distributed in such a way that partial positive and negative charges exist in different regions of the molecule. Such a molecule becomes a small dipole. Dipole moment (abbreviated μ) is the multiplicative product of the charges in a dipole (q) times the distance separating the charges (d).

$$\mu = q \times d \quad (\text{A-42})$$

Changing electric or magnetic fields cause the molecule to rotate and orient itself in alignment with the fields.

2. Theoretical Correlations

Dipole moments are related to electronegativity and geometry and can be calculated by quantum mechanical calculations.

The electric dipole moment $\vec{\rho}_e$ is typically defined in terms of point charges $q_1, q_2 \dots q_n$ located at positions $\vec{r}_1, \vec{r}_2 \dots \vec{r}_n$ by the equation

$$\vec{\rho}_e = \sum q_i \vec{r}_i \quad (\text{A-43})$$

If instead of an array of point charges, we have a continuous distribution of charge $\rho(\vec{r})$, the summation must be replaced by an integral and

$$\vec{\rho}_e = \int \rho(\vec{r}) \vec{r} d\tau \quad (\text{A-44})$$

The electric dipole moment operator that must be used with the wave functions to calculate the observable property is

$$\vec{p}_e = e \sum Z_i \vec{R}_i - e \sum \vec{r}_k \quad (\text{A-45})$$

where the first term accounts for nuclear charges and the second term the electrons.

Specifically, Z_i is the atomic number of nucleus i , R_i is internuclear separation, and r_k is electron-electron distance. Within the Born-Oppenheimer approximation the calculated electric dipole moment becomes

$$p_e = e \sum Z_i R_i - e \int \sum r_k |\psi|^2 d\Gamma \quad (\text{A-46})$$

The factor $e|\psi|^2$ is the electron density at any given point in space. These point densities are appropriately summed and combined with the nuclear charge distribution to give the dipole moment.

3. Estimation Methods

Dipole moments have been calculated for a wide range of organic compounds containing the elements C, H, N, and O using the AM1 parameterization schemes. The difference between calculated and experimental dipole moments was 0.24 ± 0.24 debye (Reference A-15). We calculated values for the electric dipole moments using the MOPAC semiempirical program of 1-carbon alkanes (Table A-11).

H. FIRE SUPPRESSION CONCENTRATION

1. Description of the Property

Fire suppression concentration is the concentration of an agent in air required to extinguish an *n*-heptane flame in the NMERI cup burners. It can be calculated by comparing volumetric flow rates of agent and air at extinguishment.

$$\text{Fire suppression conc (\%)} = [V_{\text{agent}} / (V_{\text{agent}} + V_{\text{air}})] \times 100\% \quad (\text{A-47})$$

This concentration varies slightly with the flow rate and cup burner used.

2. Theoretical Correlations

An algorithm developed by others to estimate the flame-extinguishment concentrations of halocarbons in a cup burner has been extended and refined using our cup burner data. This algorithm relates the extinguishment concentration to the number of atoms of different types and CF_3 groups.

The effectiveness of a fire suppression agent in real-world, large-scale fires depends upon deliverability of the agent, heat removal from the flames by the agent, and radical reactions that interfere with the combustion process. Both physical and chemical processes contribute to extinguishment. Physical suppression results from dilution and cooling. Cooling is provided by absorption of heat by the vaporized or gaseous material and,

TABLE A-11. CALCULATED DIPOLE MOMENTS FOR 1-CARBON HALOALKANES.

Molecule	$\mu(\text{D})$	Molecule	$\mu(\text{D})$	Molecule	$\mu(\text{D})$
CH ₃ F	1.93	CH ₂ BrCl	1.40	CBr ₂ I ₂	0.47
CH ₂ F ₂	2.04	CHClF ₂	1.69	CBrI ₃	0.38
CHF ₃	2.08	CHCl ₂ F	1.40	CHF ₂ I	1.51
CF ₄	0.00	CHBrF ₂	1.55	CHFI ₂	1.12
CH ₃ Cl	0.20	CHBr ₂ F	1.21	CHCl ₂ I	1.05
CH ₂ Cl ₂	1.50	CHBr ₂ Cl	0.99	CHClI ₂	0.89
CHCl ₃	1.16	CHBrCl ₂	1.07	CHBr ₂ I	0.89
CCl ₄	0.00	CHBrClF	1.29	CHBrI ₂	0.82
CH ₃ Br	1.48	CBr ₂ ClF	0.42	CH ₂ FI	1.52
CH ₂ Br ₂	1.32	CBrCl ₂ F	0.40	CH ₂ ClI	1.29
CHBr ₃	0.91	CBrClF ₂	0.25	CH ₂ BrI	1.22
CBr ₄	0.00	CH ₃ I	1.35	CHClFI	1.30
CClF ₃	0.59	CH ₂ I ₂	1.12	CHBrFI	1.20
CCl ₂ F ₂	0.36	CHI ₃	0.72	CHBrClI	0.97
CCl ₃ F	0.20	Cl ₄	0.00	CCl ₂ FI	0.98
CBrF ₃	1.02	CF ₃ I	1.68	CClF ₂ I	1.27
CBr ₂ F ₂	0.60	CF ₂ I ₂	1.07	CClFI ₂	0.93
CBr ₃ F	0.43	CFI ₃	0.80	CBr ₂ FI	0.78
CBrCl ₃	0.22	CCl ₃ I	0.74	CBrF ₂ I	1.05
CBr ₂ Cl ₂	0.21	CCl ₂ I ₂	0.68	CBrFI ₂	0.84
CBr ₃ Cl	0.17	CClI ₃	0.50	CBrCl ₂ I	0.63
CH ₂ ClF	1.79	CBr ₃ I	0.45	CBr ₂ ClI	0.54
CH ₂ BrF	1.68				

to a lesser extent, from evaporation of liquid agents. Larger molecules have more molecular degrees of freedom and the resulting high vapor phase heat capacities provide significant cooling action. Thermal molecular dissociation and liquid-phase heat absorption may also play a role; however, like dilution, the effects of these mechanisms are believed to be relatively small. Physical extinguishment mechanisms include

- (a) vapor-phase heat absorption
- (b) liquid-phase heat absorption
- (c) evaporative cooling
- (d) thermal dissociation
- (e) dilution of fuel and oxygen

For many applications, weight or storage (liquid) volume of agent is the critical limiting factor. For aircraft, weight is most critical (volume is also important, but to a lesser extent than weight). The volume of space for agent storage on ships is limited. Consequently, it is useful to compare the effectiveness of alternative agents not only by mole (gas volume) percent, but also by weight and liquid (storage) volume.

To calculate a weight effectiveness index, the fire suppression concentration of a candidate agent (in mole percent) is multiplied by its molecular weight (in grams/mole), and the product is divided by the product of the fire suppression concentration and molecular weight of the reference compound (Halon 1211 or 1301).

$$W = \frac{\text{conc} \times \text{MW for agent}}{\text{conc.} \times \text{MW for standard}} \quad (\text{A-48})$$

To calculate a liquid volume effectiveness index, both numerator and denominator in Equation (A-48) are converted to volume by dividing by the liquid densities of the candidate and standard material, respectively.

$$L = \frac{(\text{conc} \times \text{MW for agent} / \text{conc.} \times \text{MW for standard})}{\times (\text{liquid density of standard} / \text{liquid density of agent})} \quad (\text{A-49})$$

I. GLOBAL WARMING POTENTIAL

1. Description of the Property

The greenhouse effect is caused by the absorbance of infrared light in the "atmospheric window" (the 8-12 μm , 800-1200 cm^{-1} region). Molecules containing carbon-to-halogen bonds (C-F, C-Cl, C-Br) absorb infrared radiation in this region, causing energy that would otherwise have been lost into space to be converted into thermal (kinetic) energy of molecules in the atmosphere. The global warming potential (GWP) of a chemical is its ability to raise the mean temperature of the earth. It is measured on a per-weight basis relative to CFC-11 = 1.0. GWP is approximately the normalized product of atmospheric lifetime multiplied by temperature sensitivity. Atmospheric lifetime depends on the rate of removal by reaction with $\cdot\text{OH}$, photolysis, or other sinks. Temperature sensitivity is a measure of how much the temperature of a body of air increases for every part per billion by volume (ppbv) of an organic present. It is a quantitative measure of the infrared absorption by a molecule in the atmospheric window.

2. Theoretical Correlations

GWP is directly proportional to both atmospheric lifetime and temperature sensitivity. Table A-12 lists known lifetimes, temperature sensitivities, and GWPs of halocarbons¹ (A-18). These data were fitted to the formula

$$\text{GWP} = C \times \text{Temperature Sensitivity} \times \text{Atmospheric Life} \quad (\text{A-50})$$

and the constant C was found to have the value 0.202. Thus knowledge of any two of the three factors included in Equation (A-50) allows calculation of the third quantity. The formula shown in Equation (A-50) allowed the estimates of temperature sensitivities shown in

¹ McCulloch, A., "Update and Outlook for the AFEAS Program," Global Business Outlook for CFC Alternatives, March 12-13, 1991, West London, England.

Table A-12. An algorithm is currently under development to estimate temperature sensitivity based on calculated infrared spectra from MOPAC quantum mechanical calculations.

3. Previous Estimation Methods Used

To our knowledge no estimation methods have been used previously. Temperature sensitivities have been measured experimentally and the values used, along with atmospheric sink reaction rates, to calculate GWPs.

J. HEATS OF FORMATION AND REACTION

1. Descriptions of the Properties

The heat of formation of a substance (ΔH_f° , also called enthalpy of formation) is the thermal change involved in the formation of 1 mole of a substance from its elements. If each of the substances involved in the reaction is in its standard state and each substance is at unit activity, the thermal change is the standard heat of formation, ΔH_f° . By definition, all elements in their standard states have a heat of formation of zero. The sign of ΔH is defined to be negative if heat is evolved in the formation reaction, and positive if heat is absorbed.

2. Theoretical Correlations

The heat of formation of a substance can be calculated from heats of combustion. The heat of formation of compound X is equal to the sum of the heats of formation of the products of combustion of compound X minus the heat of combustion of compound X.

$$\Delta H_f^\circ (X) = \Delta H_f^\circ (\text{combustion products of X}) - \Delta H(X) \quad (\text{A-51})$$

A list of common combustion products of halocarbons with their heats of formation appears in Table A-13.

TABLE A-12. REPORTED LIFETIMES, TEMPERATURE SENSITIVITIES, GWPs.

Halocarbon No.	Atmospheric lifetime (yrs)	Temperature sensitivity (°C/ppbv)	GWP ^a
10	50	0.05	0.34
11	60	0.09	^b 1.00
12	120	0.13	3.10
13	400	0.1	^c 8.1
14	500	0.04	^c 4.0
20	0.7	0.04	^c 0.0057
21	1.93	^c 0.64	0.250
22	14.2	0.08	0.350
22B1	110	0.1	2.00
30	0.6	0.02	^c 0.0024
31	1.35	^c 0.92	0.250
113	90	0.12	1.40
114	200	0.14	3.90
115	400	0.12	7.50
116	500	0.08	^b 8.1
123	1.47	0.07	0.018
124	6.04	0.08	0.250
125	26.7	0.09	0.580
133a	25	^c 0.10	0.500
134a	14.4	0.07	0.270
141b	7.8	0.05	0.092
142b	17.9	0.07	0.360
143a	39.5	0.06	0.740
152a	1.56	0.04	0.030

^aRelative to CFC-11, value varies depending on model used.

^bBy definition (standard compound).

^cValue estimated using Equation (A-50).

TABLE A-13. HEATS OF FORMATION OF COMMON HALOCARBON COMBUSTION PRODUCTS.

Material	ΔH_f° (kcal/mol)
CO	-26.416
CO ₂	-93.963
1/2 H ₂ O(l)	-34.158
H ₂ O(l)	-68.317
HF ^a	-76.531
HCl ^a	-39.850
HBr ^a	-28.958
HI ^a	-13.106

^aIn dilute aqueous solution.

3. Calculation Method

The heat of formation, ΔH_f° , of a compound is fundamentally related to the energy level obtained from the Schrödinger equation. In the MOPAC program the equilibrium geometry is found by minimizing the total energy with respect to bond length, bond angle and dihedral angle. The energy of atomization of the molecule is the difference between the energy so obtained and the energy of its component atoms calculated in a way as similar as possible to the molecular computation. These atomization energies are equated to experimentally determined heats of formation at 25 °C, ΔH_f° .

The heats of formation are used with Hess's law to calculate heats of reaction, $\Delta H_{\text{rxn},298}^\circ$. The reactions of interest are those in which the halocarbons are combined with oxygen and/or water to yield CO₂ and hydrogen halides.

4. Results

Calculated and measured values of ΔH_f° for one-carbon halogenated hydrocarbons are reported in Table A-14. The heats are given in units of kcal mol⁻¹ (Reference A-15).

The reactions expected for decomposition of halogenated hydrocarbons expected in a flame environment and their corresponding heats of reaction are collected in Table A-15.

5. Reliability

In a comparison of AM1 values for ΔH_f° with experimental results it was found that for a sample of 58 hydrocarbons the average mean error was ± 5.1 kcal mol⁻¹ and that for a sample of 80 organic compounds containing nitrogen and/or oxygen the average mean error was ± 5.9 kcal mol⁻¹ (Reference A-19). For the 29 halogenated hydrocarbons in Table A-14 for which ΔH_f° values are known the average mean error is ± 5.0 kcal mol⁻¹. We conclude that the balance of the ΔH_f° values in Table A-14 have an uncertainty of ± 5.0 kcal mol⁻¹.

K. LETHAL CONCENTRATION

1. Description of the Property

Since all chemicals are toxic under some condition of exposure, it is necessary to define the conditions and quantity of exposure in order to compare the toxic characteristics of chemicals. Acute toxicity is the toxic effect produced by a single, or sometimes multiple, exposure to a chemical by any route for a short time, usually less than one day. Acute toxicity is often determined by lethality data, either levels of exposure (LC₅₀) or the dose (LD₅₀) estimated to kill 50 percent of a specific population of animals under controlled conditions. The median lethal concentration or LC₅₀ is generally used to express the acute

toxicity due to exposure to airborne chemicals. This term is distinct from the often confused median lethal dose, LD_{50} , which refers to the actual quantity of chemical that is directly applied, often orally, to the test population.

It is often convenient, although not always appropriate, to express the toxicity of a chemical by using one toxic endpoint. This method is dangerous, since chemicals often have more than one toxic endpoint that they influence, and lethality, although certainly the most definite, may not adequately define the toxicity of a chemical. Nonetheless, a commonly used value that allows direct comparisons of toxicities among chemicals is the rat 4-hour LC_{50} . This term specifies the concentration to which rats are exposed by inhalation for a 4-hour time period that kills 50 percent of the test population. Most researchers agree that the rat is the species of choice, other than primates themselves, when it is desirable to extrapolate experimental data to a human population (Reference A-20), which is usually the ultimate goal in toxicity testing. Since halon replacements are generally gaseous agents, inhalation is the most important route of exposure, although skin, eye, and oral contact may also provide potential exposure routes.

The simple determination of the LC_{50} value provides an initial comparative index for the lethal potential of a particular chemical. Table A-16 presents an approximate classification scheme of chemicals, which allows one to rate the toxicity of chemicals on a similar scale (Reference A-21).

TABLE A-14. CALCULATED AND EXPERIMENTAL HEATS OF FORMATION.

Molecule	ΔH_f° (kcal mol ⁻¹)	
	Calculated	Measured
CH ₃ F	- 60.9	-59
CH ₂ F ₂	-116.1	-108
CHF ₃	-172.5	-166
CF ₄	-225.7	-223.4
CH ₃ Cl	- 22.5	-19.6
CH ₂ Cl ₂	- 25.8	-22.9
CHCl ₃	- 29.0	-25.0
CCl ₄	- 28.1	-23.2
CH ₃ Br	- 6.2	-9.1
CH ₂ Br ₂	- 1.0	0
CHBr ₃	6.4	5.7
CBr ₄	15.9	20.1
CClF ₃	-162.6	-169.7
CCl ₂ F ₂	-107.0	-114.1
CCl ₃ F	- 60.9	64
CBrF ₃	-144.6	-155
CBr ₂ F ₂	- 74.1	-91
CBr ₃ F	- 18.0	-56
CBrCl ₃	- 14.7	-10.2
CBr ₂ Cl ₂	- 2.8	2
CBr ₃ Cl	7.4	---
CH ₂ ClF	- 65.3	-62
CH ₂ BrF	- 49.8	---
CH ₂ BrCl	- 12.6	-11
CHClF ₂	-114.2	-115.6

TABLE A-14. CALCULATED AND EXPERIMENTAL HEATS OF FORMATION
(CONTINUED).

Molecule	ΔH_f° (kcal mol ⁻¹)	
	Calculated	Measured
CHCl ₂ F	- 65.2	---
CHBrF ₂	- 96.8	---
CHBr ₂ F	- 35.6	---
CHBr ₂ Cl	- 3.7	2
CHBrCl ₂	- 15.5	-12
CHBrClF	- 49.5	---
CBr ₂ ClF	- 31.0	---
CBrCl ₂ F	- 45.3	---
CBrClF ₂	- 90.0	-105
CH ₃ I	5.7	3.7
CH ₂ I ₂	21.4	28
CHI ₃	37.8	28
Cl ₄	54.2	---
CF ₃ I	-132.6	-141
CF ₂ I ₂	- 51.2	---
CFI ₃	13.8	---
CCl ₃ I	- 2.6	---
CCl ₂ I ₂	19.9	---
CClI ₃	38.9	---
CBr ₃ I	25.8	---
CBr ₂ I ₂	35.5	---
CBrI ₃	44.9	---
CHF ₂ I	- 84.2	---
CHFI ₂	- 12.2	---
CHCl ₂ I	- 3.2	---

TABLE A-14. CALCULATED AND EXPERIMENTAL HEATS OF FORMATION
(CONCLUDED).

Molecule	ΔH_f° (kcal mol ⁻¹)	
	Calculated	Measured
CHCl ₂	19.1	---
CHBr ₂ I	17.1	---
CHBrI ₂	27.6	---
CH ₂ FI	- 37.4	---
CH ₂ ClI	- 0.3	---
CH ₂ BrI	10.4	---
CHClFI	- 37.1	---
CHBrFI	-23.6	---
CHBrClI	7.8	---
CCl ₂ FI	- 33.3	---
CClF ₂ I	- 78.0	---
CClFI ₂	- 8.2	---
CBr ₂ FI	- 7.2	---
CBrF ₂ I	- 62.6	---
CBrFI ₂	3.4	---
CBrCl ₂ I	8.6	---
CBr ₂ ClI	18.1	---

TABLE A-15. HEATS OF REACTION FOR ALL ONE-CARBON HALOALKANES.

Reaction		$\Delta H^\circ_{\text{rxn}}$ (kcal mol ⁻¹)
$\text{CH}_3\text{F(g)} + 3/2 \text{O}_2 \text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HF(g)} + \text{H}_2\text{O(g)}$	-155.1
$\text{CH}_2\text{F}_2\text{(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HF(g)}$	-106.4
$\text{CHF}_3\text{(g)} + 1/2 \text{O}_2 + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 3 \text{HF(g)}$	- 56.4
$\text{CF}_4\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 4 \text{HF(g)}$	- 9.5
$\text{CH}_3\text{Cl(g)} + 3/2 \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + \text{H}_2\text{O(g)}$	-151.4
$\text{CH}_2\text{Cl}_2\text{(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HCl(g)}$	-112.3
$\text{CHCl}_3\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 3 \text{HCl(g)}$	- 73.4
$\text{CCl}_4\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 4 \text{HCl(g)}$	- 38.6
$\text{CH}_3\text{Br(g)} + 3/2 \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{H}_2\text{O(g)}$	-154.3
$\text{CH}_2\text{Br}_2\text{(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)}$	-110.4
$\text{CHBr}_3\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 3 \text{HBr(g)}$	- 68.6
$\text{CBr}_4\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 4 \text{HBr(g)}$	- 29.0
$\text{CClF}_3\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + 3 \text{HF(g)}$	- 30.5
$\text{CCl}_2\text{F}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HCl(g)} + 2 \text{HF(g)}$	- 44.0
$\text{CCl}_3\text{F(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 3 \text{HCl(g)} + \text{HF(g)}$	- 47.9
$\text{CBrF}_3\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr} + 3 \text{HF(g)}$	- 35.2
$\text{CBr}_2\text{F}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + 2 \text{HF(g)}$	- 50.0
$\text{CBr}_3\text{F(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 3 \text{HBr(g)} + \text{HF(g)}$	- 50.6
$\text{CBrCl}_3\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 3 \text{HCl(g)}$	- 38.6
$\text{CBr}_2\text{Cl}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + 2 \text{HCl(g)}$	- 37.2
$\text{CBr}_3\text{Cl(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 3 \text{HBr(g)} + \text{HCl(g)}$	- 19.0
$\text{CH}_2\text{ClF(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + \text{HF(g)}$	-115.0
$\text{CH}_2\text{BrF(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HF(g)}$	-117.1
$\text{CH}_2\text{BrCl(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HCl(g)}$	-112.2
$\text{CHClF}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + 2 \text{HF(g)}$	- 72.5
$\text{CHCl}_2\text{F(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HCl(g)} + \text{HF(g)}$	- 79.4
$\text{CHBrF}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 2 \text{HF(g)}$	- 85.1

TABLE A-15. HEATS OF REACTION FOR ALL ONE-CARBON HALOALKANES
(CONTINUED).

Reaction	$\Delta H^{\circ}_{\text{rxn}}$ (kcal mol ⁻¹)
$\text{CHBr}_2\text{F(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + \text{HF(g)}$	- 91.3
$\text{CHBr}_2\text{Cl(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + \text{HCl(g)}$	- 71.9
$\text{CHBrCl}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 2 \text{HCl(g)}$	- 73.5
$\text{CHBrClF(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HCl(g)} + \text{HF(g)}$	- 81.7
$\text{CBr}_2\text{ClF(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + \text{HCl(g)} + \text{HF(g)}$	- 51.1
$\text{CBrCl}_2\text{F(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 2 \text{HCl(g)} + \text{HF(g)}$	- 50.2
$\text{CBrClF}_2\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HCl(g)} + 2 \text{HF(g)}$	- 47.6
$\text{CH}_3\text{I(g)} + 3/2 \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HI(g)} + \text{H}_2\text{O(g)}$	-151.3
$\text{CH}_2\text{I}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HI(g)}$	-103.2
$\text{CHI}_3\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 3 \text{HI(g)}$	- 55.5
$\text{CI}_4\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 4 \text{HI(g)}$	- 7.9
$\text{CF}_3\text{I(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 3 \text{HF(g)} + \text{HI(g)}$	- 32.2
$\text{CF}_2\text{I}_2\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HF(g)} + 2 \text{HI(g)}$	- 43.3
$\text{CFI}_3\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HF(g)} + 3 \text{HI(g)}$	- 37.8
$\text{CCl}_3\text{I(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 3 \text{HCl(g)} + \text{HI(g)}$	- 35.8
$\text{CCl}_2\text{I}_2\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HCl(g)} + 2 \text{HI(g)}$	- 30.0
$\text{CClI}_3\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + 3 \text{HI(g)}$	- 20.8
$\text{CBr}_3\text{I(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 3 \text{HBr(g)} + \text{HI(g)}$	- 24.0
$\text{CBr}_2\text{I}_2\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + 2 \text{HI(g)}$	- 18.8
$\text{CBrI}_3\text{(g)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 3 \text{HI(g)}$	- 13.5
$\text{CHF}_2\text{I(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HF(g)} + \text{HI(g)}$	- 74.3
$\text{CHF}_2\text{I(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HF(g)} + 2 \text{HI(g)}$	- 75.9
$\text{CHCl}_2\text{I(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HCl(g)} + \text{HI(g)}$	- 70.9
$\text{CHClI}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + 2 \text{HI(g)}$	- 65.0
$\text{CHBr}_2\text{I(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + \text{HI(g)}$	- 64.5
$\text{CHBrI}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 2 \text{HI(g)}$	- 60.1
$\text{CH}_2\text{FI(g)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{HF(g)} + \text{HI(g)}$	-114.6

TABLE A-15. HEATS OF REACTION FOR ALL ONE-CARBON HALOALKANES (CONCLUDED).

Reaction		$\Delta H^{\circ}_{\text{rxn}}$ (kcal mol ⁻¹)
$\text{CH}_2\text{ClI(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + \text{HI(g)}$	-109.6
$\text{CH}_2\text{BrI(g)} + \text{O}_2\text{(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HI(g)}$	- 106.9
$\text{CHClFI(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + \text{HF(g)} + \text{HI(g)}$	- 79.2
$\text{CHBrFI(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HF(g)} + \text{HI(g)}$	- 79.4
$\text{CHBrClI(g)} + 1/2 \text{O}_2\text{(g)} + \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HCl(g)} + \text{HI(g)}$	- 68.6
$\text{CCl}_2\text{FI(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HCl(g)} + \text{HF(g)} + \text{HI(g)}$	- 47.3
$\text{CClF}_2\text{I(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + 2 \text{HF(g)} + \text{HI(g)}$	- 44.7
$\text{CClFI}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HCl(g)} + \text{HF(g)} + 2 \text{HI(g)}$	- 44.1
$\text{CBr}_2\text{FI(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO(g)} + 2 \text{HBr(g)} + \text{HF(g)} + \text{HI(g)}$	- 46.5
$\text{CBrF}_2\text{I(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 2 \text{HF(g)} + \text{HI(g)}$	- 46.7
$\text{CBrFI(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + \text{HF(g)} + 2 \text{HI(g)}$	- 42.3
$\text{CBrCl}_2\text{I(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + \text{HBr(g)} + 2 \text{HCl(g)} + \text{HI(g)}$	- 33.7
$\text{CBr}_2\text{ClI(g)} + 2 \text{H}_2\text{O(g)}$	$\rightarrow \text{CO}_2\text{(g)} + 2 \text{HBr(g)} + \text{HCl(g)} + \text{HI(g)}$	- 29.8

2. Values

Unfortunately, relatively few halocarbons have rat 4-hour LC_{50} values determined because this test is costly and many animals are needed and sacrificed for its determination. For example, just recently a rat 4-hour LC_{50} value was determined for Halon 1211 (Reference A-22), but prior to 1990, no research laboratory had ever performed the necessary tests to determine this value. Most lethality data for halocarbons have been determined using mice as test species. Accordingly, the data available to generate a QSAR to predict lethality in mammals must utilize mouse data, and indeed, Davies and associates formulated an algorithm correlating acute lethality in mice with the influence of acidic hydrogen and nonpolar interaction (Reference A-23). Fitting the mouse

TABLE A-16. TOXICITY CLASSES.

Toxicity Rating	Descriptive Term	LD ₅₀ ^a (wt/kg)	LC ₅₀ ^b (ppm)
1	Extremely Toxic	1 mg or less	< 10
2	Highly Toxic	1 - 50 mg	10 - 100
3	Moderately Toxic	50 - 500 mg	100 - 1000
4	Slightly Toxic	0.5 - 5 g	1,000-10,000
5	Practically Nontoxic	5 - 15 g	10,000 - 100,000
6	Relatively Harmless	15 g or more	> 100,000

^aSingle oral dose in rats.^b4-hr inhalation in rats.

30-minute LC₅₀ values with P_o, the nonpolar interaction, and H, a term describing the hydrogen bond proton donor properties yields the Equation (A-52):

$$\log_e LC_{50} = 6.16 (\pm 0.17) - 1.94 (\pm 0.08) P_o - 0.70 (\pm 0.04) H \quad (A-52)$$

Details on these two terms (P_o and H) were provided earlier in Section A (Anesthetic Dose). The error in the LC₅₀ values are slightly higher than for the anesthetic dose and was taken to be 0.14 - 0.20 log_e units.

L. LIQUID DENSITY

Liquid density is given by

$$\rho = M/V \quad (A-53)$$

where ρ is the liquid density at the boiling point, M is the molar mass, and V is the molar volume of liquid at the boiling point. The molar volume is estimated by adding up the factors shown in Table A-17.

TABLE A-17. MOLAR VOLUME ADDITIVITY FACTORS.

Atom	Increment (mL/g-mol)
C	7
H	7
F	10.5
Cl	24.5
Br	31.5
I	38.5

If a double bond is present, an extra increment of 7 is added. The average error of this method is ± 3.4 percent. For example, to estimate the density of liquid HCFC-123 (CHCl_2CF_3) at its boiling point,

$$\begin{aligned}\rho &= M/V = (153 \text{ g/mol}) / [(2 \times 7) + (1 \times 7) + (2 \times 24.5) + (3 \times 10.5) \text{ mL/g-mol}] \\ &= 153/101.5 \text{ g/mL} = 1.51 \text{ g/mL}\end{aligned}$$

The actual density of HCFC-123 near its boiling point is 1.47 g/mL.

Liquid density decreases slightly with increasing temperature, as the molar volume increases because of increased molecular motion. A formula to estimate the liquid density at a particular temperature (knowing the boiling point and the liquid density at the boiling point) is given in Equation (A-54).

$$\rho = M\rho_b[3-2(T/T_b)^{0.31}] \quad (\text{A-54})$$

where ρ is the liquid density at the desired temperature, M is the molar mass, ρ_b is the liquid density at the boiling point, T is the temperature in kelvins, and T_b is the boiling point in kelvins.

M. LIQUID VISCOSITY

1. Description of the Property

Viscosity is the internal resistance to flow exhibited by a fluid. It is also the ratio of shearing stress to rate of shear. The viscosity of a liquid is one poise if a force of one dyne per square centimeter causes two parallel liquid surfaces one square centimeter in area and one centimeter apart to traverse each other at a velocity of 1 cm/sec. Common units include centipoise, poise, and Pascal-seconds. Conversion factors among these units are

$$1 \text{ poise} = 100 \text{ centipoise}$$

$$1 \text{ Pascal-second} = 10 \text{ poise} = 1000 \text{ centipoise}$$

Viscosity may be measured either by dropping a small metal sphere through a container of the liquid and noting the time to fall (the Saybolt method) or by placing the liquid in a glass tube provided with a small outlet and recording the time to escape.

Kinematic viscosity (in centistokes, 1 stoke = 100 centistokes) is viscosity in centipoises divided by the liquid density at the same temperature. Kinematic viscosity is measured by recording the time for a measured quantity of liquid to flow by gravity through a standard capillary tube.

A more complex molecular organization generally results in higher viscosity. Water has a viscosity of 0.0100 poise or 1.00 centipoise at 20 °C. Molasses may have a kinematic viscosity of several hundred centistokes, and a heavy lubricating oil may be near 100 centistokes.

2. Previous Estimation Methods Used

A rough estimate of the viscosity of a pure liquid at its boiling point can be obtained from the modified Arrhenius equation

$$\mu_b = 0.01\rho_b^{0.5} \quad (\text{A-55})$$

where μ_b is the viscosity at the boiling point in mNs/m² and ρ_b is the density at the boiling point in kg/m³. A more accurate value can be obtained from Souders' equation, if a reliable value for density is available or if it can be estimated with sufficient accuracy (Reference A-24).

$$\log(\log 10\mu) = (I/M)\rho \times 10 - 2.9 \quad (\text{A-56})$$

where μ is the viscosity in mNs/m², M is the molecular weight, ρ is the density at the required temperature in kg/m³, and I is Souders' index, estimated by adding the group contributions given in Table A-18.

TABLE A-18. CONTRIBUTIONS FOR I IN SOUDERS' EQUATION.

Atom, Bond, or Group	Contribution
H	2.7
C	50.2
Cl	60
Br	79
I	110
R ₂ CH-X	6
R ₂ CH-CHR ₂	8
R ₄ C	10

The accuracy of the predictions made by this method for organic liquids is usually ± 10 percent.

3. Temperature Dependence

Viscosity is greatly affected by temperature, especially for liquids composed of large complex molecules such as asphalt or heavy oils.

N. MOLAR REFRACTION

The molar refraction, R , is defined as

$$R = [(n^2-1)/(n^2+2)][M/d] \quad (\text{A-57})$$

where n is the refractive index, M is the molecular weight, d is the density in grams per cm^3 , and $[M/d]$ is the volume occupied by one mole of the compound. The units of R are cm^3 . To a first approximation, R is independent of temperature or physical state, and it provides an approximate measure of the actual total volume (without free space) occupied by the molecules in one mole of the substance. The molar refraction is also related to the polarizability α by the Lorenz-Lorentz equation

$$R = 4\pi N\alpha/3 \quad (\text{A-58})$$

where N is Avogadro's number. For a very large number of compounds R may be approximated for a molecule by adding the contributions of the constituent atoms shown in Table A-19 (References A-25 and A-26).

TABLE A-19. ATOMIC CONTRIBUTIONS TO MOLAR REFRACTION.

Atom	Contribution to Refraction
C (sp ³)	2.418
H	1.100
F	0.81
Cl	5.967
Br	8.865
I	13.900

For example, the molar refraction of CHClF_2 (HCFC-22) can be calculated as follows:

$$\begin{aligned}
 &1 \text{ carbon} + 1 \text{ hydrogen} + 1 \text{ chlorine} + 2 \text{ fluorine} \\
 &= 2.418 + 1.100 + 5.967 + 2(0.81) = 11.11 \text{ cm}^3
 \end{aligned}
 \tag{A-59}$$

Similarly, for the slightly more complex molecule CHCl_2CF_3 (HCFC-123):

$$\begin{aligned}
 &2 \text{ carbons} + 1 \text{ hydrogen} + 2 \text{ chlorines} + 3 \text{ fluorines} = \\
 &2(2.418) + 1.100 + 2(5.967) + 3(0.81) = 20.30 \text{ cm}^3
 \end{aligned}
 \tag{A-60}$$

O. OCTANOL-WATER PARTITION COEFFICIENT AND AQUEOUS SOLUBILITY

1. Description of the Property

The octanol-water partition coefficient (K_{ow}) is a measure of the relative solubility of a substance in a relative nonpolar phase (1-octanol) versus an aqueous phase. It is a specific type of distribution coefficient (K_D). 1-Octanol was chosen as the standard because of its similarity in polarity to biological lipids.

2. Empirical Correlations

A linear relationship has been observed between the molar refraction and the logarithm of the n-octanol/water partition coefficient for 50 compounds including 9 haloalkanes (Reference 25). The equation for this relationship is

$$\log K_{ow} = 0.0753R + 0.43 \quad (A-61)$$

We refitted this equation for haloalkanes and obtained

$$\log K_{ow} = 0.0986R - 0.236 \quad (A-62)$$

with $r^2 = 0.90$ for 19 degrees of freedom. The standard deviation in this fit is 0.4 in $\log K_{ow}$, corresponding to a factor of 2.7 in K_{ow} . Thus, once the molar refraction is known, K_{ow} can be estimated within a factor of three.

K_{ow} is related to the aqueous solubility of a given compound (Reference A-27). The existence of such a relationship makes intuitive sense because K_{ow} and aqueous solubility are related phenomena. The equation relating the two is

$$\ln K_{ow} = 7.494 - \ln C^s \quad (A-63)$$

where C^s is the molar solubility in mol/m^3 . To convert molar solubility to ppm, C^s is multiplied by one thousand times the molecular weight.

$$S = (1.797 \times 10^6 \times M)/K_{ow} \quad (A-64)$$

where S is solubility in ppm and M is molecular weight.

P. OZONE-DEPLETION POTENTIAL

1. Description of the Property

Ozone-depletion potential is a quantitative estimate of the ability of a compound to destroy stratospheric ozone. It is expressed as a ratio to the ODP of CFC-11 (defined as 1.00). At present, no experimental method for measuring the ODP of a compound exists. The values are rigorously calculated on supercomputers using one- or two-dimensional atmospheric models. The calculations require as input the experimentally-determined photolytic cross sections and rates of reaction with hydroxyl radical.

2. Theoretical Correlations

The relationship between atmospheric lifetime and ODP has been examined, and a theoretically supportable formula has been developed. ODP depends on the fraction of molecules surviving to reach the stratosphere and the number of chlorine or bromine atoms delivered per molecule. We have developed a simplified algorithm for estimating ODP which has the form

$$\text{ODP} = A \times F_s \times F_r \quad (\text{A-65})$$

where A is a normalizing constant, F_s is a survival factor (the fraction of molecules surviving transport to the stratosphere), and F_r is a reactivity factor depending on the number of chlorine and bromine atoms in the molecule. If τ is the tropospheric lifetime of a compound, the fraction surviving to reach the stratosphere is $\exp(-c/\tau)$ where c_2 is a constant representing transit time through the troposphere to the tropopause. This transit time is approximately the same for all the molecules considered because the main transport mechanism is eddy diffusion (physical mixing). The reactivity factor can be approximated as $(n_{\text{Cl}} + c_3 n_{\text{Br}})$ where n_{Cl} and n_{Br} are the numbers of chlorine and bromine atoms in the molecule and c_3 is a factor accounting for the greater ozone destruction by bromine relative to chlorine. Substituting these into the above equation gives

$$\text{ODP} = c_1 \exp(-c_2/\tau)(n_{\text{Cl}} + c_3 n_{\text{Br}}) \quad (\text{A-66})$$

Fitting of the constants for non-brominated compounds ($c_3 = 0$) using rigorously calculated ODPs and estimated tropospheric lifetimes for hydrogen-containing H(C)FCs gives $c_1 = 0.0443$ and $c_2 = 2.90$ with $r^2 = 0.72$ for 8 degrees of freedom. This equation, taken with the equation estimating tropospheric lifetime, allows estimation of ODPs for all one- and two-carbon H(C)FCs.

The input required for rigorous calculations of atmospheric lifetimes and ODPs consists of photolytic cross sections and rate constants for reaction with $\cdot\text{OH}$. Although it may be possible to estimate these data in some cases, it is preferable (and will give much more accurate calculations of lifetimes and ODPs) to have experimental data. In certain cases some literature data are available. When literature data are not available, a few grams of material will need to be obtained and experimental values of photolytic cross sections and rate constants with $\cdot\text{OH}$ will need to be determined.

It is necessary to gain insight into the influences of the following structural features for algorithm development and future screening of candidate agents:

Br vs. Cl

Br vs. F

2 Br vs. 1 Br

geminal vs. vicinal

2 C vs. 1 C

2 H vs. 1 H

This information will help determine which isomer among several has the shorter atmospheric lifetime and lower ODP.

The compounds chosen for calculation of rigorous ODPs must be chosen carefully because the calculations are time-consuming and computer-intensive. Most importantly, a range of structures is desired that will allow extrapolation of ODPs by

algorithm. Therefore, a range of one-, two-, and three-carbon compounds should be included, some with one Br, some with two Br, and one or more with one Br and one Cl.

One or more compounds with two hydrogens and a fully halogenated compound with a geminal dibromide (for easy photolysis, e. g. 1,1-dibromo-1,2,2,2-tetrafluoroethane, an isomer of Halon 2402) should be included. In addition, if there is reason to believe that an HBFC has low toxicity, perhaps it should be included.

Table A-20 lists candidate compounds considered for calculations, with properties including availability of the compound and whether rates of reaction with OH and photolytic cross sections have been reported in the literature. Knowledge of rigorously calculated ODPs on this list of compounds will assist the development of related chemicals.

If these chemicals are unavailable or experimental values for rate constants with $\cdot\text{OH}$ or photolytic cross sections do not exist for any of the primary candidates, then secondary candidates will be substituted.

To include CHBrF_2 , CHBr_2F , CH_2BrF , and CHBrClF would provide a lot of valuable information for one-carbon compounds. For a range of two-carbon compounds the following (among others) should be considered:

- 2-bromo-1,1,1,2-tetrafluoroethane
- 1-bromo-1,1,2,2-tetrafluoroethane
- 1-bromo-1,2,2-trifluoroethane
- 1,2-dibromo-1,2,2-trifluoroethane
- 1-bromo-2-chloro-1,1,2-trifluoroethane
- 1,1-dibromo-1,2,2,2-tetrafluoroethane

TABLE A-20. CANDIDATE COMPOUNDS FOR ODP CALCULATIONS.

Formula	HBFC No.	Halon No.	Rate of Reaction with Hydroxyl	Photolytic Cross Section	Availability	Comments
CHBr ₂ F	21B2	1102				Short life, low ODP expected; both H and geminal dibromide
CH ₂ BrF	31B1	1101				May require custom synthesis
CHBrClF	21B1	1111			Probably	Short life and low ODP expected; has H & geminal bromochloro.
CH ₂ BrCl	30B1	1011			Yes	CB, in current use.
CH ₂ Br ₂ ^a	30B2	1002			Yes	
CHBrCl ₂	20B1	1021				May require custom synthesis.
CF ₃ CHBrCl ^b	123aB1	2311				Halothane
CF ₃ CHBrF ^b	124B1	2401			Yes	ICI may calculate.
CF ₃ CHBr ₂	123aB2	2302			Yes	Short life, low ODP expected; both H and geminal dibromide.
CF ₃ CH ₂ Br	133B1	2301			Yes	
CF ₃ CBr ₂ F	114aB2	2402				Isomer of 2402, geminal dibromo
CF ₂ ClCHBrF	123B1	2311			Yes	
CBrF ₂ CHBrF	123B2	2302			Yes	
CBrF ₂ CHClF	123bB1	2311			Yes	
CH ₂ Cl ₂ ^a	30	102			Yes	No Br
C ₆ BrF ₅	--	--			Yes	Aromatic

^aPhotolytic cross section data are available in the literature.^bRate of reaction with Hydroxyl and photolytic cross section data are available in the literature.

Q. POLARIZABILITY

1. Description of the Property

Polarizability (denoted α) is the ability of the electron cloud in a molecule to become displaced in response to an external electric field such as that created by a full or partial charge from a neighboring ion or molecule. It is the electric dipole moment induced per unit of electric intensity.

Polarizability is a measure of the response of the electrostatic potential V of a molecule to the application of an external electrostatic field $\vec{E}$. Expressed as a multipole expansion of the electric dipole moment

$$\vec{p}_e(\vec{E}) = \vec{p}_e(O) + \vec{\alpha} \cdot \vec{E} + 1/2 \vec{E} \cdot \vec{\beta} \cdot \vec{E} + \dots \quad (\text{A-67})$$

Here the α_{ij} are the components of the electric dipole polarizability tensor

$$\vec{\alpha} = \begin{matrix} & \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \begin{matrix} \rightarrow \\ \alpha \end{matrix} = & \alpha_{21} & \alpha_{22} & \alpha_{23} \\ & \alpha_{31} & \alpha_{32} & \alpha_{33} \end{matrix}$$

Molecules respond to a dynamic external electric field differently than they do to a static field, making it necessary to distinguish between static and dynamic polarizabilities. Since polarizability is frequency dependent, care must be used in comparing theoretical and experimental values. They may result from measurements at different frequencies.

2. Calculation Method

The procedure for calculating the polarizability in MOPAC is via perturbation of the Hamiltonian matrix elements. That is, in the LCAO-SCF formulation the matrix eigenvalue problem

$$h^F C_k = E_k S C_k \quad (\text{A-68})$$

must be solved.

If an electric field is applied to the molecule, the effect is to perturb the Hamiltonian operator, yielding the new eigenvalue problem

$$(h^F + \Delta) C_k = E_k S C_k \quad (\text{A-69})$$

the difference between the perturbed $\Delta H_f^{\circ'}$ and unperturbed ΔH_f° heats of formation is

$$\Delta H_f^{\circ'} = \Delta H_f^{\circ} - Vq - dV/dx p_e - (d^2V/dx^2 \alpha) \quad (\text{A-70})$$

That is, $\Delta H_f^{\circ'}$ in the field is the field-free ΔH_f° , less the electric potential times the charge q , the electric field gradient times any dipole p_e , and the square of the electric field gradient times the polarizability. The result is converted to polarization volume and is expressed in cubic angstroms (References A-28 and A-29). The MNDO parameterization must be used in this calculation.

3. Results

Calculated values of the polarization volumes α' for the halomethanes are collected in Table A-21.

These are the infinite frequency polarization volumes, α'_{∞} . This is a more convenient unit than polarizability, α . The relation between the two is $\alpha' = \alpha/4\pi\epsilon_0$, where

ϵ_0 is the permittivity of free space and has the value $8.854 \times 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1}$. As a consequence, polarizability α has the units $\text{J}^{-1}\text{C}^2\text{m}^2$.

4. Reliability

Since the polarization volumes are calculated from heats of formation, the relative uncertainties of the two sets of values should be similar. This means that the α'_∞ reported in Table A-21 have 1σ uncertainties of approximately $\pm 0.5 \text{ \AA}^3$.

R. VAPOR HEAT CAPACITY

1. Description

The heat capacity C of a substance is the proportionality constant that relates the heat transferred Q to the temperature change in the substance under consideration

$$Q = C (T_2 - T_1) \quad (\text{A-71})$$

For a rigorous definition, only infinitesimal changes are appropriate, so

$$C = DQ/dT \quad (\text{A-72})$$

where the D in DQ emphasizes that C is an inexact quantity. Furthermore, it is necessary to specify whether the measurements were performed under conditions of constant pressure or constant volume:

$$C_p = (DQ/\partial T)_p \quad (\text{A-73})$$

$$C_v = (DQ/\partial T)_v \quad (\text{A-74})$$

TABLE A-21. MOPAC CALCULATED POLARIZATION VOLUMES.

Molecule	α' , Å ³	Molecule	α' , Å ³	Molecule	α' , Å ³
CH ₃ F	2.506	CH ₂ BrCl	3.224	CBr ₂ I ₂	7.046
CH ₂ F ₂	1.593	CHClF ₂	2.586	CBrI ₃	7.363
CHF ₃	1.664	CHCl ₂ F	3.333	CHF ₂ I	3.580
CF ₄	1.725	CHBrF ₂	3.158	CHFI ₂	5.072
CH ₃ Cl	3.981	CHBr ₂ F	4.276	CHCl ₂ I	4.684
CH ₂ Cl ₂	2.871	CHBr ₂ Cl	4.668	CHClI ₂	5.370
CHCl ₃	3.940	CHBrCl ₂	4.333	CHBr ₂ I	5.265
CCl ₄	5.131	CHBrClF	3.826	CHBrI ₂	5.610
CH ₃ Br	2.292	CBr ₂ ClF	5.529	CH ₂ FI	3.167
CH ₂ Br ₂	3.525	CBrCl ₂ F	5.021	CH ₂ ClI	3.598
CHBr ₃	4.942	CBrClF ₂	4.300	CH ₂ BrI	3.888
CBr ₄	6.485	CH ₃ I	2.676	CHClFI	4.217
CClF ₃	2.713	CH ₂ I ₂	4.270	CHBrFI	4.660
CCl ₂ F ₂	3.676	CHI ₃	5.974	CHBrClI	5.007
CCl ₃ F	4.475	Cl ₄	7.700	CCl ₂ FI	5.394
CBrF ₃	3.327	CF ₃ I	3.732	CClF ₂ I	4.708
CBr ₂ F ₂	4.934	CF ₂ I ₂	5.833	CClFI ₂	6.300
CBr ₃ F	5.972	CFI ₃	7.100	CBr ₂ FI	6.323
CBrCl ₃	5.571	CCl ₃ I	5.894	CBrF ₂ I	5.361
CBr ₂ Cl ₂	5.950	CCl ₂ I ₂	6.596	CBrFI ₂	6.701
CBr ₃ Cl	6.256	CClI ₃	7.195	CBrCl ₂ I	6.258
CH ₂ ClF	2.315	CBr ₃ I	6.752	CBr ₂ ClI	6.544
CH ₂ BrF	2.762				

For an ideal gas the relationship between the two heat capacities is

$$C_p = C_v + nR \quad (\text{A-75})$$

where n is the number of moles of the substance and R is the gas constant. C_p is the property most commonly measured in a laboratory and reported in tabulations of heat capacity while C_v is the more fundamental property from a theoretical perspective.

2. Calculation Method

Bulk thermodynamic quantities, including vapor-phase heat capacities, can be calculated from molecular properties provided sufficient information is known about the molecules (Reference A-30). The requisite information consists of moments of inertia, molecular mass, vibrational frequencies, ground electronic state degeneracy, and temperature. The first three of these data sets come directly from the MOPAC calculations, the ground state degeneracy is taken as unity (the possibility of the involvement of electronically excited states at high temperature is neglected), and the final C_v computations are carried out for a desired set of temperatures.

The constant volume heat capacity is

$$C_v = (\partial U / \partial T)_v = -(1/kT^2)(\partial U / \partial \beta)_v \quad (\text{A-76})$$

where U is the internal energy, and $\beta = 1/kT$ where k is the Boltzmann constant and T is the absolute temperature. From statistical thermodynamics

$$U = -(1/q)(\partial q / \partial \beta) \quad (\text{A-77})$$

where q is the molecular partition function. It is the product of individual energy mode partition functions

$$q = q^t q^r q^v q^e \quad (\text{A-78})$$

in which t, r, v, e refer to translational, rotational, vibrational, and electronic energy modes. The individual mode partition functions for a gas of noninteracting molecules are given by

$$q^t = (2\pi mkT/h^2)^{3/2} RT/P \quad (A-79)$$

$$q^r = (\Pi^{1/2}) [(2kT/\hbar^2) I_A I_B I_C]^{1/2} \quad (A-80)$$

$$q^v = \prod_i^{3N-6} [1/(1 - \exp(-\hbar\nu_i/kT))] \quad (A-81)$$

$$q^e = q \quad (A-82)$$

where T is a rotational symmetry number, P is pressure, I_i are moments of inertia, $\hbar = h/c$, and q is the electronic state degeneracy.

In the MOPAC program calculations of $C_p(T)$ are carried out for molecules where internal rotations are absent and the substance is taken to be an ideal gas (Reference A-31). The program as distributed does not calculate thermodynamic quantities, including heat capacities of molecules with either free or hindered internal rotations. Thus, heat capacity calculations were not carried out on two-carbon halogenated hydrocarbons.

3. Vapor Heat Capacity Algorithm

In theory, the vapor heat capacity of a nonlinear molecule has a contribution of $(3/2)R$ from translation, $(3/2)R$ from rotation, and a maximum at high temperatures of $(3n-6)R$ from vibration, where n is the number of atoms in the molecule. The sum of these contributions is $(3n-3)R$. This simple model therefore predicts that all methanes will have the same vapor heat capacity (12R), as will all ethanes (21R), and so on (Table A-22).

TABLE A-22. THEORETICAL HEAT CAPACITY AT CONSTANT PRESSURE.

Type of Compound	n	C _p (Units of R)
Methanes	5	12
Ethanes	8	21
Propanes	11	30
Butanes	14	39

This simple model does not account for differences in vibrational energies based on bond strengths. A more sophisticated algorithm would allow differing vibrational contributions based on bond types. Since the number of C-H bonds in a molecule equals the number of hydrogen atoms (and similarly for F, Cl, and Br), and the number of C-C bonds equals the number of carbons minus one, this algorithm would take the form

$$\text{heat capacity} = A + B \cdot n_H + C \cdot n_F + D \cdot n_{Cl} + E \cdot n_{Br} + F \cdot (n_C - 1) \quad (\text{A-83})$$

where A represents the (constant) contribution of translational and rotational motions, B is the contribution of each C-H bond, C is the contribution of each C-F bond, D is the contribution of each C-Cl bond, E is from each C-Br bond, and F is from each C-C bond. This algorithm makes the assumption that all bonds of each type (e.g., C-H) are equal in strength.

A survey of the NMERI HALOCARBON DATABASE showed that 94 chemicals have reported vapor heat capacities. Multiple regression analysis using the robust Andrew's sine method gave Equation (A-84).

$$C_{\text{vap}} = 26.00 + 9.18N_H + 14.02N_F + 15.14N_{Cl} + 15.91N_{Br} + 23.27(N_C - 1) \text{ J/mole-K} \quad (\text{A-84})$$

The quality of fit was $R^2 = 0.947$ for 94 compounds (89 degrees of freedom). Iodinated compounds were not included in this algorithm because insufficient vapor heat capacity data were available for iodo carbons.

This simple model does not account for differences in vibrational energies based on bond strengths. A more sophisticated algorithm would allow differing vibrational contributions based on bond types. At present we are estimating vapor heat capacities using MOPAC.

The temperature dependence of the heat capacity of an ideal gas is the series expansion

$$C_p = A + BT + CT^2 + DT^3 \quad (\text{A-85})$$

where C_p is the heat capacity of the ideal gas, A, B, C, and D are characteristic constants for the particular compound, and T is the absolute temperature in kelvins (Reference A-32). Constants for 26 haloalkanes of 4 carbons or less are listed. This information can also be used to calculate the heat absorbed in heating a gas at constant pressure.

$$\begin{aligned} \Delta H &= \int C_p dT = \int (A + BT + CT^2 + DT^3) dT \\ &= (AT + BT^2/2 + CT^3/3 + DT^4/4) |_{T_2/T_1} \end{aligned} \quad (\text{A-86})$$

This equation is useful for calculating the physical contribution of agents to flame extinguishment in cup-burner tests by heat removal.

Several group contribution methods have been developed for the estimation of these constants. The values from one source for group contributions to ideal gas heat capacities are given in Table A-23.

TABLE A-23. GROUP CONTRIBUTIONS TO HEAT CAPACITIES, kJ/mol-K.

Group	A	B x 10 ²	C x 10 ⁴	D x 10 ⁶
-CH	2.5485	8.9740	-0.3567	0.004752
-CH ₂ -	1.6518	8.9447	-0.5012	0.0187
-CH-	-14.7516	14.3020	-1.1791	0.03356
>C<	-24.4131	18.6493	-1.7619	0.05288
-F	6.0215	1.4453	-0.0444	-0.00014
-Cl	12.8373	0.8885	-0.0536	0.00116
-Br	11.5577	1.9808	-0.1905	0.0060
-I	13.6703	2.0520	-0.2257	0.00746

4. Reliability

As a test of the computation method, heat capacity calculations were carried out on 27 compounds containing primarily C, H, N, and O atoms; a few Cl- and S-containing molecules were included. The average error of C_p° (298 K) was 0.63 cal mol⁻¹ K⁻¹. At higher temperatures (however, below temperatures at which dissociation becomes appreciable) the agreement improves. Specifically, at 900 K the absolute error dropped to 0.35 cal mol⁻¹ K⁻¹ (1.69 percent). Eventually the rigid-rotor harmonic-oscillator approximation leads to greater deviations from reality.

S. VIBRATIONAL FREQUENCIES

1. Description

In all molecules the number of coordinates required to specify the locations of the constituent atoms at any time are three times the number of atoms in the molecule, 3N. Of these 3N coordinates, or degrees of freedom, three may be used to describe the location of the center of mass; that is, they refer to translation of the molecule as a unit.

Furthermore, three degrees of freedom are required to describe the rotation of a nonlinear molecule (two for a linear molecule). The balance, $3N-6$ for nonlinear and $3N-5$ for linear molecules, are internal degrees of freedom, that is, motions of atoms with respect to one another within a molecule, or molecular vibrations. These may be given in any coordinate system, but it is most helpful to express these as a set of $3N-6$ (or $3N-5$) independent and mutually orthogonal atomic displacements called normal coordinates. An important feature of vibrational motion in the normal coordinate is that it behaves as a simple harmonic oscillator. These coordinates may be loosely grouped as stretches, bends, wags, and twists of the chemical bonds in the molecule.

In addition to the displacement, the coordinates are characterized by the distinctive vibrational frequency of the normal coordinate, $\tilde{\nu}$, expressed in wave numbers, cm^{-1} . The relationships between common measures of wavelength are

$$\lambda = 1/\tilde{\nu} = c/\nu \quad (\text{A-87})$$

where λ = wavelength, $\tilde{\nu}$ = wave number, c = speed of light, and ν = vibrational frequency. Absorption of one quantum of radiation by vibrating molecules occurs in the infrared region of the spectrum.

The strength or the ability of any of these normal modes to absorb radiation is important. This is commonly related to a frequency dependent absorption coefficient, $\alpha(\nu)$, defined by the integrated form of Beer's law as

$$\alpha(\nu) = (1/\rho l) \ln I_0/I \quad (\text{A-88})$$

where ρ is the number density of the sample in molecules cm^{-3} , l is the cell length, I_0 is the intensity of the incident radiation, and I is the radiation intensity after passing through the absorption cell.

An absorption band for any transition covers a range of frequencies. The total intensity of the band is obtained by measuring $\alpha(\tilde{\nu})$ over the absorption region and determining the integrated absorption coefficient, $\tilde{A}$,

$$\tilde{A} = \int_{\text{overband}} \alpha(\tilde{\nu}) d\tilde{\nu} \quad (\text{A-89})$$

2. Calculation Method

Calculations of the nine normal vibrational frequencies of one-carbon halogenated hydrocarbons were made as one of the options available in the MOPAC program. A variation of the method developed by McIver and Komornicki (Reference A-33) to search potential surfaces for transition states is used for normal coordinate analysis. In this procedure, the quantum mechanical calculation of heat formation yields a hyperdimensional potential energy surface. In the Cartesian coordinate system force constants for small displacements of each atom are obtained as the second derivative of the potential surface centered at the geometry of minimum energy (Reference A-34). The matrix of second derivatives is mass weighted and used in the Wilson FG procedure (Reference A-35) to arrive at both the frequencies and the normal modes.

The integrated intensity $\tilde{A}_{01}$ for the fundamental transition on any vibration is given by

$$\tilde{A}_{01} = 8\pi^3 \rho p / 3hc \tilde{\nu}_{01} |\mu_{01}|^2 \quad (\text{A-90})$$

where h is Planck's constant, c is the speed of light, $\tilde{\nu}_{01}$ is frequency of the fundamental in cm^{-1} , and $|\mu_{01}|$ is the transition dipole moment. The transition dipole moment comes from the quantum mechanical calculations and is defined by

$$|\mu_{01}| = \int_{-\infty}^{\infty} \psi_0^* \mu \psi_1 dq \quad (\text{A-91})$$

where ψ_0^* is the complex conjugate of the wave function of the ground vibrational level, ψ_1 is the wave function of the first excited vibrational level, and μ is the dipole along the normal coordinate q .

3. Reliability

The results with the MINDO/3 parameterization have been compared with experiments for a large number of compounds containing C,H,N, and O atoms. For CH stretches, the calculated frequencies systematically lie about 15 percent high, while all other frequencies cluster about the experimental values with a standard deviation of 10 percent (Reference A-34). No study of the reliability of CX (X = halogen) frequencies has been reported, but the values are likely reliable to ± 10 percent.

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APPENDIX B

SELECTED REFERENCES ON PREDICTION OF PHYSICAL PROPERTIES

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APPENDIX C

TWO SIMPLE SERIES FOR DETERMINATION OF EMPIRICAL CORRELATIONS

The properties studied for empirical correlations are listed below:

- Boiling point
- Density
- Dielectric constant
- Dipole moment
- Heat of combustion
- Heat of vaporization
- Liquid heat capacity
- Melting point
- Refractive index
- Thermal conductivity
- Vapor heat capacity
- Vapor pressure
- Viscosity

It was expected that in related series of compounds, many of these properties would show smoothly-curving trends for these properties, and many pairs of properties would show empirical correlations.

Among these compounds numerous series of related chemicals exist. Forty series involving one-carbon compounds are listed below. Each series is described by two phrases, one describing which atom(s) is being substituted on the parent compound, and one describing the initial and final molecular formulas for the series.

1. Successively replacing hydrogens with one type of halogen
 - a. CH_3F , CH_2F_2 , CHF_3 , CF_4 (substituting F for H, C1F1 H3 to F3)
 - b. CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 (substituting Cl for H, C1Cl1 H3 to Cl3)
 - c. CH_3Br , CH_2Br_2 , CHBr_3 , CBr_4 (substituting Br for H, C1Br1 H3 to Br3)
 - d. CH_3I , CH_2I_2 , CHI_3 , CI_4 (substituting I for H, C1I1 H3 to I3)

2. Replacing a halogen with another halogen
 - a. CH_3F , CH_3Cl , CH_3Br , CH_3I (constant CH_3 , C1H3 F to I)
 - b. CH_2F_2 , CH_2Cl_2 , CH_2Br_2 , CH_2I_2 (constant CH_2 , C1H2 (F to I)2)
 - c. CHF_3 , CHCl_3 , CHBr_3 , CHI_3 (constant CH, C1H1 (F to I)3)
 - d. CF_4 , CCl_4 , CBr_4 , CI_4 (constant C, C1 (F to I)4)

3. Successive substitution of one particular halogen for another
 - a. CF_4 , CF_3Cl , CF_2Cl_2 , CFCl_3 , CCl_4 (substituting Cl for F, C1 F4 to Cl4)
 - b. CF_4 , CF_3Br , CF_2Br_2 , CFBr_3 , CBr_4 (substituting Br for F, C1 F4 to Br4)
 - c. CF_4 , CF_3I , CF_2I_2 , CFI_3 , CI_4 (substituting I for F, C1 F4 to I4)
 - d. CCl_4 , CCl_3Br , CCl_2Br_2 , CClBr_3 , CBr_4 (substituting Br for Cl, C1 Cl4 to Br4)
 - e. CCl_4 , CCl_3I , CCl_2I_2 , CClI_3 , CI_4 (substituting I for Cl, C1 Cl4 to I4)
 - f. CBr_4 , CBr_3I , CBr_2I_2 , CBrI_3 , CI_4 (substituting I for Br, C1 Br4 to I4)

4. Substitution of one halogen for another, with one hydrogen present
 - a. CHF_3 , CHCl_3 , CHBr_3 , CHI_3 (constant CH, C1H1 (F to I)3)
 - b. CHF_3 , CHF_2Cl , CHFCl_2 , CHCl_3 (substituting Cl for F, C1H1 F3 to Cl3)
 - c. CHF_3 , CHF_2Br , CHFBr_2 , CHBr_3 (substituting Br for F, C1H1 F3 to Br3)
 - d. CHF_3 , CHF_2I , CHFCl_2 , CHI_3 (substituting I for F, C1H1 F3 to I3)
 - e. CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3 (substituting Br for Cl, C1H1 Cl3 to Br3)
 - f. CHCl_3 , CHCl_2I , CHClI_2 , CHI_3 (substituting I for Cl, C1H1 Cl3 to I3)

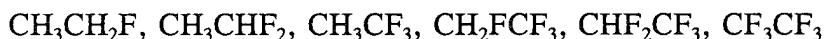
- g. $\text{CHBr}_3, \text{CHBr}_2\text{I}, \text{CHBrI}_2, \text{CHI}_3$ (substituting I for Br, C1H1 Br3 to I3)
5. Substitution of one halogen for another, with two hydrogens present
- $\text{CH}_2\text{F}_2, \text{CH}_2\text{Cl}_2, \text{CH}_2\text{Br}_2, \text{CH}_2\text{I}_2$ (constant CH_2 , C1H2 (F to I)2)
 - $\text{CH}_2\text{F}, \text{CH}_2\text{ClF}, \text{CH}_2\text{BrF}, \text{CH}_2\text{FI}$ (constant CH_2F , C1H2F1 F to I)
 - $\text{CH}_2\text{ClF}, \text{CH}_2\text{Cl}_2, \text{CH}_2\text{BrCl}, \text{CH}_2\text{ClI}$ (constant CH_2Cl , C1H2Cl1 F to I)
 - $\text{CH}_2\text{BrF}, \text{CH}_2\text{BrCl}, \text{CH}_2\text{Br}, \text{CH}_2\text{BrI}$ (constant CH_2Br , C1H2Br1 F to I)
 - $\text{CH}_2\text{FI}, \text{CH}_2\text{ClI}, \text{CH}_2\text{BrI}, \text{CH}_2\text{I}$ (constant CH_2I , C1H2I1 F to I)
6. Three mixed halogens, one hydrogen
- $\text{CHClF}_2, \text{CHCl}_2\text{F}, \text{CHBrClF}, \text{CHClFI}$ (constant CHFCl , C1H1Cl1F1 F to I)
 - $\text{CHBrF}_2, \text{CHBrClF}, \text{CHBr}_2\text{F}, \text{CHBrFI}$ (constant CHBrF , C1H1Br1F1 F to I)
 - $\text{CHBrClF}, \text{CHBrCl}_2, \text{CHBr}_2\text{Cl}, \text{CHBrClI}$ (constant CHBrCl , C1H1Br1Cl1 F to I)
7. One halogen constant, three others change together
- $\text{CF}_4, \text{CCl}_3\text{F}, \text{CBr}_3\text{F}, \text{CFI}_3$ (constant CF, C1F1 (F to I)3)
 - $\text{CClF}_3, \text{CCl}_4, \text{CBr}_3\text{Cl}, \text{CClI}_3$ (constant CCl, C1Cl1 (F to I)3)
 - $\text{CBrF}_3, \text{CBrCl}_3, \text{CBr}_4, \text{CBrI}_3$ (constant CBr, C1Br1 (F to I)3)
 - $\text{CF}_3\text{I}, \text{CCl}_3\text{I}, \text{CBr}_3\text{I}, \text{CI}_4$ (constant CI, C1I1 (F to I)3)
8. Three mixed halogens constant, one halogen changes
- $\text{CBrClF}_2, \text{CBrCl}_2\text{F}, \text{CBr}_2\text{ClF}, \text{CBrClFI}$ (constant CBrClF , C1Br1Cl1F1 F to I)
 - $\text{CClF}_2\text{I}, \text{CCl}_2\text{FI}, \text{CBrClFI}, \text{CClFI}_2$ (constant CClFI , C1Cl1F1 F to I)
 - $\text{CBrClFI}, \text{CBrCl}_2\text{I}, \text{CBr}_2\text{ClI}, \text{CBrClI}_2$ (constant CBrClI , C1Br1Cl1I1 F to I)

9. Two identical halogens constant, other two halogens change together

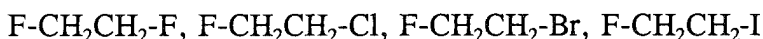
- a. CF_4 , CCl_2F_2 , CBr_2F_2 , CF_2I_2 (constant CF_2 , C1F2 (F to I)²)
- b. CCl_2F_2 , CCl_4 , CBr_2Cl_2 , CCl_2I_2 (constant CCl_2 , C1Cl2 (F to I)²)
- c. CBr_2F_2 , CBr_2Cl_2 , CBr_4 , CBr_2I_2 (constant CBr_2 , C1Br2 (F to I)²)
- d. CF_2I_2 , CCl_2I_2 , CBr_2I_2 , Cl_4 (constant Cl_2 , C1I2 (F to I)²)

There are 217 possible noniodinated derivatives of ethane that contain at least one halogen atom. Some representative series are listed below. Similar trends can be drawn for Cl, Br, or I in place of F.

1. Successive substitution of F for H



2. Substitution of H with X



3. Other Series

