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## MAIN GROUP COMPOUNDS AS EXTINGUISHANTS

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## PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico, for the Department of Defense, Strategic Environmental Research and Development Program (SERDP), under Defense Supply Service-Washington (DSS-W) Contract HQ0038-7350-0009, NMERI Number 8-33380. This is Project 4D/5/8 under the Next-Generation Fire Suppression Technology Program (NGP).

The Start Date was 19 February 1998, and the End Date is 31 March 1999. The Technical Program Manager is Dr. Richard G. Gann, National Institute of Standards and Technology; the Contracting Officer's Technical Representative (COTR) is Dr. Ronald S. Sheinson, Naval Research Laboratory, and the NMERI Principal Investigator (PI) is Dr. J. Douglas Mather. Dr. Robert E. Tapscott served as the Deputy PI.

Gabriel Juarez and Maya M. Garcia were apprentices under the National Aeronautics and Space Administration (NASA) SHARP Plus Program.

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## SUMMARY

### A. TASK OBJECTIVE

The objective was to evaluate the potential of compounds other than simple halocarbons and transition metal compounds as replacements for halon fire extinguishing agents.

### B. GENERAL METHODOLOGY

This project requires the assessment of liquid or gaseous compounds of main group elements (compounds containing elements from the s and p blocks of the periodic table—Groups IA, IIA, IIIB, IVB, VB, VIB, VIIB, and VIIIB) as halon replacements. Excluded are halocarbons, amines, ethers, and silicon compounds, which have been examined extensively elsewhere. This report, which includes the objectives, methodology, results, important findings and conclusions, and implications for further research, is the final project deliverable. Of particular importance in this effort is an assessment of the potential of various chemical families and their derivatives to provide compounds as Halon 1301 substitutes and the development of a list of potential compounds.

### C. TECHNICAL RESULTS

With few exceptions, compounds of the s block elements (the alkali metals and alkaline earths—Groups IA and IIA) are solids and do not meet a primary requirement for materials considered here (that the compounds be gases or liquids). Most of the compounds which have halogens (Group VIIB) as a primary constituents and which could be considered as halon replacements are either halocarbons, amines, or ethers (which are excluded) or contain other non-carbon main group elements and are considered with those elements. The only non-halogen, non-transition metal elements that appear to provide any significant catalytic fire suppression capabilities are the alkali metals, tin, lead, and phosphorus.

#### D. IMPORTANT FINDINGS AND CONCLUSIONS

With one major exception, the results of the search have been disappointing. Few materials based on main group elements with potentially acceptable physical (primarily, volatility) and toxicological properties have been identified. The lowest molecular weight materials (i.e., the materials with the highest volatilities) often have hydrogen or halogen atoms directly attached to non-carbon atoms. The former (containing hydrogen) are often flammable, and the latter (containing halogens) are usually toxic (owing to hydrolysis). Both often have low stabilities. Moreover, few elements provide catalytic fire suppression capabilities, and compounds of most of those do not meet the requirements of this study. A major exception is fluoroalkyl phosphorus compounds, which hold significant promise despite their relatively low volatility.

#### E. SIGNIFICANT HARDWARE DEVELOPMENTS

The only hardware development made in this project was the addition of a mass flow controller for the air flow in existing cup burners.

#### F. SPECIAL COMMENTS

None.

#### G. IMPLICATIONS FOR FURTHER RESEARCH

Fluoroalkylphosphorus compounds offer the most promise as main group element halon alternatives (as defined in this project).

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## LIST OF ABBREVIATIONS

AAWG	Advanced Agent Working Group
CCOD ID	CGET Chemical Options Database Identification Number
CGET	Center for Global Environmental Technologies
COTR	Contracting Officer's Technical Representative
DEMP	diethyl methylphosphonate
DIMP	diisopropyl methylphosphonate
DMMP	dimethyl methylphosphonate
IMP	isopropyl methylphosphonate
ISO	International Standards Organization
MPA	methylphosphonic acid
NASA	National Aeronautics and Space Administration
NGP	Next-Generation Fire Suppression Technology Program
NIST	National Institute of Standards and Technology
NMERI	New Mexico Engineering Research Institute
PI	Principal Investigator
SERDP	Strategic Environmental Research and Development Program
SLM	Standard Liters/Minute
TFEP	tris(2,2,2-trifluoroethyl)phosphite
TMP	trimethylphosphate
USAF	United States Air Force

## LIST OF UNITS AND SYMBOLS

C	concentration
J	Joule
K	Kelvin
$\log_{10}$	logarithm to the base 10
mol	mole
$P_b$	external pressure at boiling point
p	vapor pressure
R	ideal gas constant
T	temperature
$T_b$	boiling point temperature
$T_c$	Trouton's constant
vol%	percent by gas volume
$^{\circ}\text{C}$	degrees Celcius
$\Delta H_r$	enthalpy of reaction
$\Delta H_{\text{vap}}$	enthalpy of vaporization
$\Delta S_{\text{vap}}$	molar entropy of vaporization

## SECTION I. INTRODUCTION

### A. OBJECTIVE

The objective was to evaluate the potential of compounds other than simple halocarbons and transition metal compounds as replacements for halon fire extinguishing agents. Though not specifically stated in the requirements, only compounds that are not solids at room temperature are targeted.

### B. SCOPE

This project requires the assessment of liquid or gaseous compounds of main group elements (compounds containing elements from the s and p blocks of the periodic table—Groups IA, IIA, IIIB, IVB, VB, VIB, VIIB, and VIIIB) as halon replacements. Excluded are halocarbons, amines, ethers, and silicon compounds, which have been examined extensively elsewhere. Of particular importance is an assessment of the potential of various chemical families and their derivatives to provide compounds as Halon 1301 substitutes and the development of a list of potential compounds.

### C. APPROACH

Much of the information acquired on candidate compounds and related chemicals has been added to the CGET Chemical Options Database<sup>©</sup> [1]. Those chemicals that appear in this database are assigned a CGET Chemical Options Database Identification Number (CCOD ID), and this number is given in this report where appropriate.

### D. BACKGROUND

Past work under the United States Air Force (USAF) and the Advanced Agent Working Group (AAWG) has performed an assessment of the fire suppressant potential of compounds in all elemental families [2]. As a result of this initiative, it was recommended that tropodegradable bromocarbons [3], silicon compounds [4], phosphorus compounds [5], and metal compounds [6]

receive particular attention. A large number of additional main group chemicals were, however, identified as having some potential promise. Due to severe funding and time limitations, no work was carried out to identify derivatives and evaluate these additional compounds.

A significant amount of work has been performed that allows a comparison of flame suppression for compounds of main group elements with that of halocarbons, which have been more widely studied. McHale gives a good overview of work in this area up to 1969 [7].

Some results from this present project have been reported at conferences [8, 9, 10].

## SECTION II. EVAPORATION EQUILIBRIUM AND RATES

### A. VOLATILITY

Only compounds that are not solids at room temperature are targeted under this specific project. Many, if not most, of the liquids found in this study are liquids with relatively high boiling points. A major criterion for use of such compounds is the ability to evaporate and fill a space to the desired concentration within the time required for extinguishment. Thus, evaporation properties must be taken into account during compound review and selection. There are two areas that must be considered—evaporation equilibrium and evaporation rate.

### B. EVAPORATION EQUILIBRIUM

The first question that must be answered is whether a given compound can achieve the required extinguishment concentration upon discharge given sufficient time for evaporation to occur. This question, which considers only evaporation equilibrium, is relatively easy since only thermodynamics are involved in the analysis. The logarithm of the ratio of the vapor pressure ( $p$ ) at two different temperatures  $T_2$  and  $T_1$  (in absolute units) can be estimated from Equation 1 (the Clausius-Clapeyron equation), where  $R$  is the ideal gas constant and  $\Delta H_{\text{vap}}$  is the heat of vaporization.\* This equation is based on the assumption that (1)  $\Delta H_{\text{vap}}$  is temperature independent and (2) the vapor is an ideal gas. The ratio of  $\Delta H_{\text{vap}}/T_b$ , where  $T_b$  is the boiling point temperature, is equal to the molar entropy of vaporization  $\Delta S_{\text{vap}}$  at the boiling point. For closely related compounds,  $\Delta S_{\text{vap}}$  at the boiling point is nearly constant with a value of  $t_c$ , Trouton's constant (Equation 2). Thus, by selecting  $T_1$  as the boiling point ( $T_b$ ) at, for example, 1 atmosphere pressure (i.e.,  $p_1 = 760$  Torr), one can estimate the vapor pressure at some other temperature and develop an approximate vapor pressure/temperature curve if  $t_c$  is known.

$$\log_{10}(p_2/p_1) = (\Delta H_{\text{vap}} (T_2 - T_1) / 2.302585RT_2T_1) \quad [1]$$

---

\*Throughout this report, numbers accompanying equations are placed in brackets and numbers accompanying reactions are placed in parentheses.

$$\Delta H_{\text{vap}}/T_b = \Delta S_{\text{vap}} \approx t_c \quad [2]$$

The two equations can be combined to simplify the estimation. For a boiling point  $T_b$  in K at a pressure  $P_b$ , Equation 3, where Trouton's constant  $t_c$  in units of J/K-mol is a variable to be determined for a particular family of compounds, is obtained.

$$p_2 = P_b 10^{*(0.05221065)t_c[1-(T_b/T_2)]} \quad [3]$$

For example, if  $t_c$  is taken to be equal to 88 J/K-mol, which holds for many compounds, one can estimate that the vapor pressure at 25 °C for a compound with a boiling point of  $T_b = 50$  °C at 760 Torr is 313 Torr. Table 1 gives the estimated vapor pressures as a function of boiling point and ambient temperature. From vapor pressure values, one can calculate the maximum concentration possible. For one atmosphere total pressure, the equilibrium (maximum possible) volume fractions are  $p_2/760$  for  $p_2$  in Torr. These values, converted to percent, are given in Table 2. Similar tables can be prepared for other pressures. Note that this analysis does not say how fast the equilibrium concentration will be reached. It only gives the maximum theoretically possible.

TABLE 1. ESTIMATED VAPOR PRESSURE (TORR) VERSUS BOILING POINT AND AMBIENT TEMPERATURE FOR TROUTON'S CONSTANT 88 J/K-MOL.

Boiling Pt., °C	Ambient Temperature, °C												
	-60	-50	-40	-30	-20	-10	0	10	20	25	30	40	50
-60	760	1221	1883	2803	4044	5673	7763	10391	13635	15512	17573	22285	27848
-50	463	760	1196	1814	2663	3795	5270	7152	9504	10879	12396	15896	20073
-40	282	473	760	1174	1753	2539	3578	4922	6625	7629	8744	11339	14469
-30	171	294	483	760	1154	1698	2429	3387	4618	5350	6168	8088	10429
-20	104	183	307	492	760	1136	1649	2331	3219	3752	4351	5769	7517
-10	64	114	195	318	500	760	1119	1605	2244	2631	3069	4115	5419
0	39	71	124	206	329	508	760	1104	1564	1845	2165	2936	3906
10	24	44	79	133	217	340	516	760	1090	1294	1527	2094	2815
20	14	28	50	86	143	228	350	523	760	908	1077	1494	2029
30	9	17	32	56	94	152	238	360	530	636	760	1065	1463
40	5	11	20	36	62	102	161	248	369	446	536	760	1054
50	3	7	13	23	41	68	110	171	257	313	378	542	760
60	2	4	8	15	27	46	74	117	179	220	267	387	548
70	1	3	5	10	18	30	51	81	125	154	188	276	395
80	1	2	3	6	12	20	34	56	87	108	133	197	285

TABLE 2. ESTIMATED MAXIMUM CONCENTRATION (VOL%) VERSUS BOILING POINT AND AMBIENT TEMPERATURE FOR TROUTON'S CONSTANT 88 J/K-MOL AND 1 ATMOSPHERE PRESSURE.

Boilin Pt., °C	Ambient Temperature, °C													
	-60	-50	-40	-30	-20	-10	0	10	20	25	30	40	50	
-60	100													
-50	61	100												
-40	37	62	100											
-30	23	39	64	100										
-20	14	24	40	65	100									
-10	8	15	26	42	66	100								
0	5	9	16	27	43	67	100							
10	3	6	10	18	29	45	68	100						
20	2	4	7	11	19	30	46	69	100					
30	1	2	4	7	12	20	31	47	70	84	100			
40	1	1	3	5	8	13	21	33	49	59	71	100		
50	0	1	2	3	5	9	14	22	34	41	50	71	100	
60	0	1	1	2	4	6	10	15	24	29	35	51	72	
70	0	0	1	1	2	4	7	11	16	20	25	36	52	
80	0	0	0	1	2	3	5	7	11	14	17	26	37	

We can also calculate the maximum allowable boiling point ( $T_b$ ) that can achieve a given concentration ( $C$ ) for various ambient temperatures,  $T_2$ . Equation 4 gives the calculation for temperatures in K,  $P_b$  in Torr, and  $t_c$  in J/K-mol. Table 3 gives the estimated maximum boiling point that can achieve concentrations from 1 vol% to 20 vol% for a Trouton constant of 88 J/K-mol. The data are plotted in Figure 1. Figure 2 gives a simplified illustration (some data have been omitted).

$$T_b = [1 - (\text{Log}(760C/100P_b)/0.05221065t_c)]T_2 \quad [4]$$

TABLE 3. ESTIMATED MAXIMUM BOILING POINT THAT CAN ACHIEVE A GIVEN CONCENTRATION.

Conc. %	Ambient Temperature, °C											
	-60	-50	-40	-30	-20	-10	0	10	20	30	40	50
1	33	47	61	76	90	105	119	133	148	162	176	191
2	19	33	46	60	74	87	101	115	128	142	156	169
3	11	24	37	51	64	77	91	104	117	130	144	157
4	5	18	31	44	57	70	83	96	109	122	135	148
5	0	13	26	39	52	65	77	90	103	116	129	142
6	-3	9	22	35	47	60	73	85	98	111	123	136
7	-6	6	19	31	44	56	69	81	94	106	119	131
8	-9	3	16	28	40	53	65	78	90	102	115	127
9	-11	1	13	25	38	50	62	74	87	99	111	124
10	-14	-1	11	23	35	47	59	72	84	96	108	120
11	-16	-3	9	21	33	45	57	69	81	93	105	117
12	-17	-5	7	19	31	43	55	67	79	91	103	115
13	-19	-7	5	17	29	41	53	65	77	88	100	112
14	-20	-9	3	15	27	39	51	63	74	86	98	110
15	-22	-10	2	14	25	37	49	61	73	84	96	108
16	-23	-11	0	12	24	36	47	59	71	83	94	106
17	-24	-13	-1	11	22	34	46	57	69	81	92	104
18	-25	-14	-2	9	21	33	44	56	68	79	91	102
19	-27	-15	-3	8	20	31	43	54	66	78	89	101
20	-28	-16	-5	7	19	30	42	53	65	76	88	99

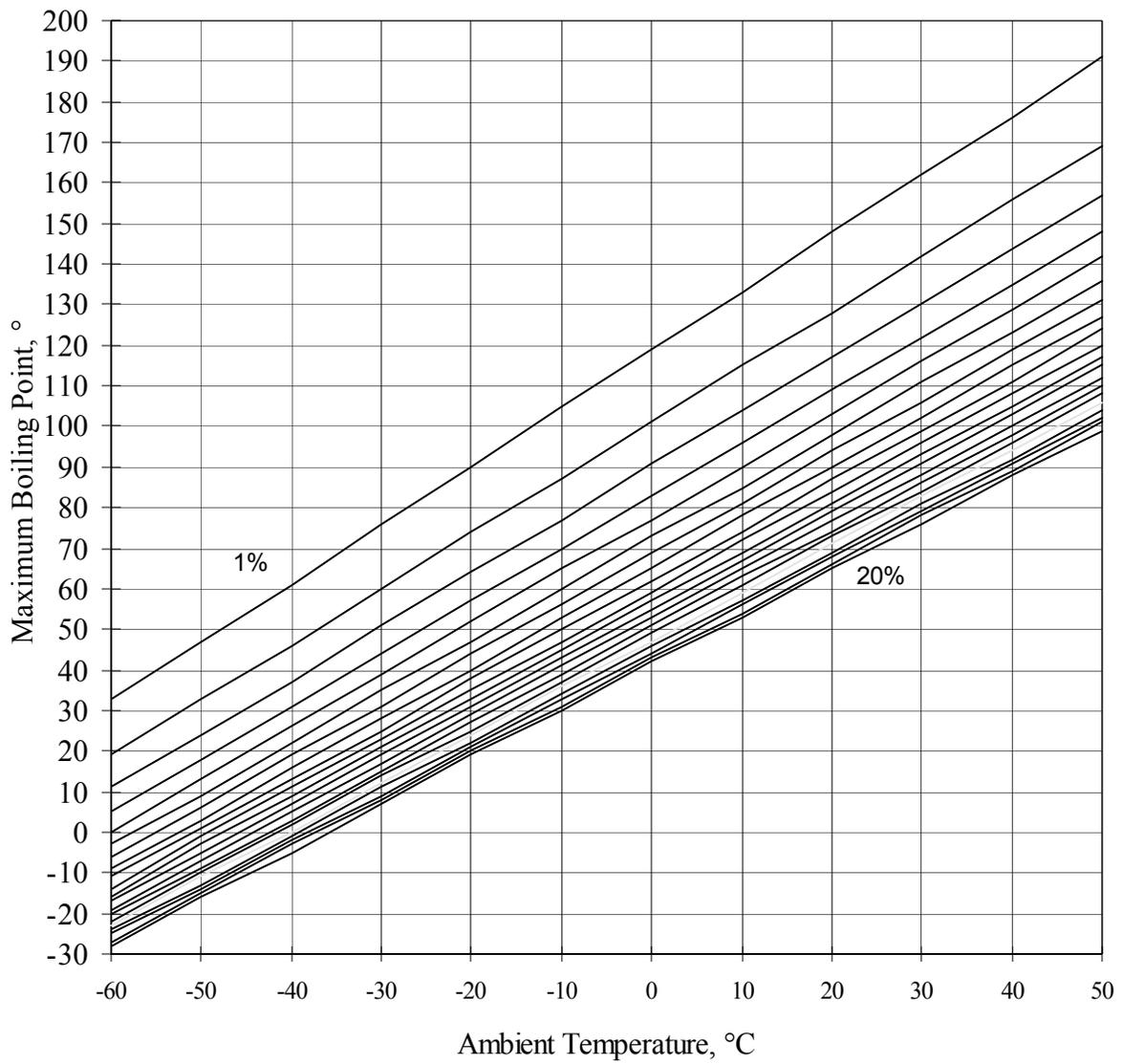


Figure 1. Estimated Maximum Boiling Points That Can Achieve Given Concentrations as Function of Ambient Temperature.

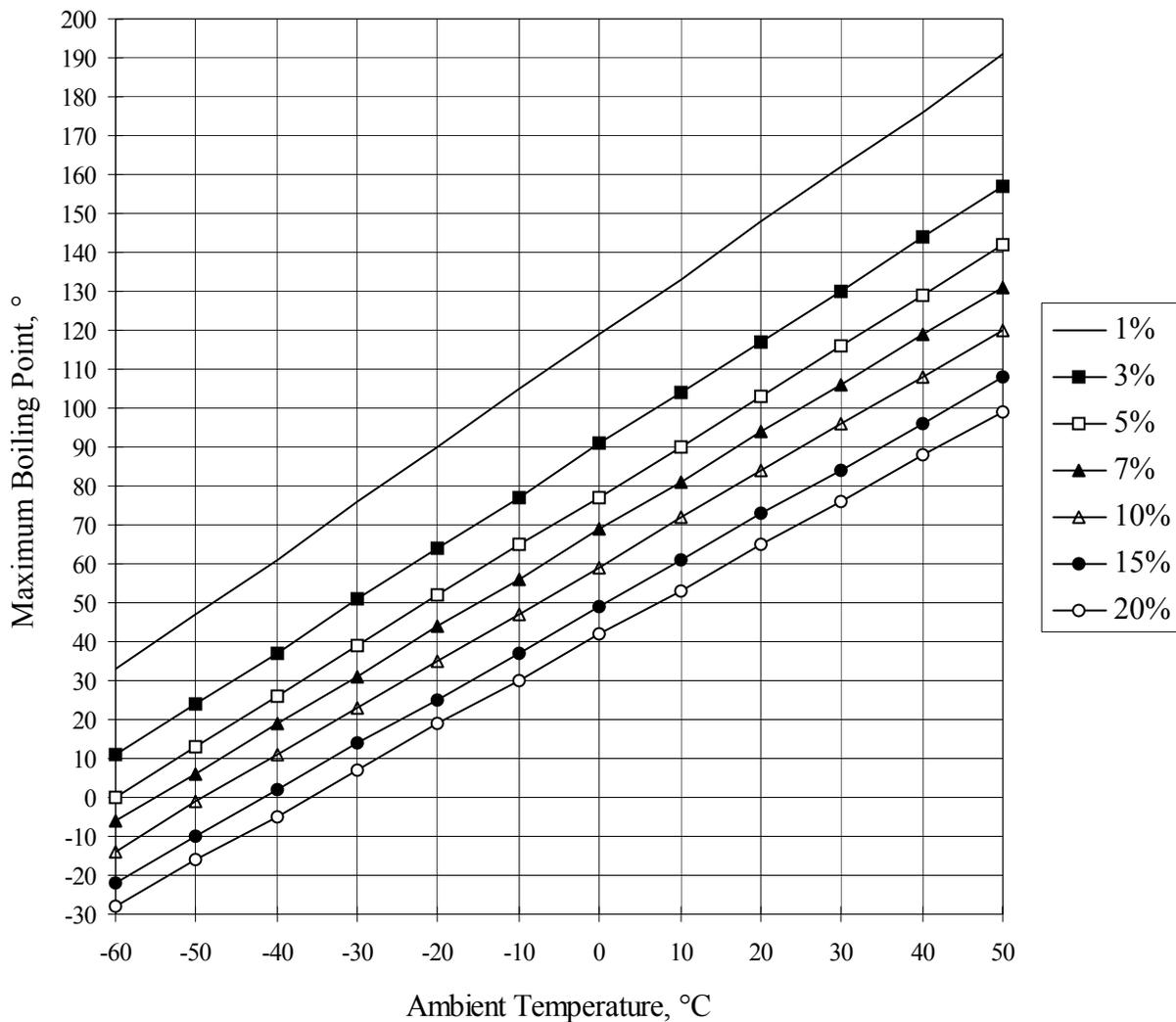


Figure 2. Estimated Maximum Boiling Points That Can Achieve Given Concentrations as Function of Ambient Temperature (Simplified), Calculated for  $t_c = 88 \text{ J/K}\cdot\text{mol}$ .

### C. EVAPORATION RATE

Calculation (or estimation) of evaporation rates are much more difficult than calculation of equilibrium agent concentrations. Here, we present an overview of some of the things that must be considered. In the simplest case, a spherical droplet of fire suppressant agent of radius  $r$  is ejected into stagnant, completely unsaturated air at velocity  $U_0$ . The rate of evaporation as a function of droplet radius and the time for complete evaporation is of interest. It is assumed that the temperature of the droplet is the same as its surroundings, and that the temperature at the surface of the droplet does not change as the droplet evaporates. While neither of these

conditions is true, considering temperature changes is too complex for a simple analysis. The following uses cgs units.

1. Fick's Law

Fick's first law for one-dimensional diffusion relates the flux ( $J$  in  $\text{g/s-cm}^2$ ) of a vapor through a gaseous medium to the concentration gradient  $dc/dx$ , where  $c$  is the concentration ( $\text{g/cm}^3$ ) and  $x$  is the direction of diffusion (Equation 5).

$$J = -D \frac{dc}{dx} \quad [5]$$

$D$ , the diffusion coefficient of the vapor in  $\text{cm}^2/\text{sec}$ , is a function of the agent and the ambient conditions. Kinetic theory shows that for ideal gases of density  $\rho$  of rigid spherical molecules having a molecular mass  $m$  and a diameter  $\sigma$ , the diffusion coefficient is given by Equation 6, where  $k$  is the Boltzmann constant and  $T$  is the temperature [11].

$$D = \frac{3 (\pi mkT)^{1/2}}{8 \pi \sigma^2 \rho} \quad [6]$$

Setting the density  $\rho = Pm/kT$ , one obtains Equation 7, which shows that the diffusion coefficient is proportional to  $T^{3/2}$  and inversely proportional to the pressure  $P$  for this idealized gas composed of hard-spheres. It is also inversely proportional to the square root of the molecular mass  $m$  and to the square of the molecular diameter  $\sigma$ . Real gases, of course, show significant deviations from this relationship, which may be modified to take into account actual molecular interactions.

$$D = \frac{3}{8} \frac{(kT)^{3/2}}{\pi^{1/2} \sigma^2 P m^{1/2}} \quad [7]$$

Continuing to use the hard-sphere model, one can relate the diffusion coefficient to the coefficient of viscosity ( $\eta$ ,  $\text{g/cm-s}$ ), the heat capacity per molecule ( $c_v$ ,  $\text{g-cm}^2/\text{s}^2\text{-}^\circ\text{C}$ , =  $C_v/N_0$ , where  $N_0$  is Avogadro's number), and the coefficient of thermal conductivity ( $\lambda$ ,  $\text{g-cm/s}^3\text{-}^\circ\text{C}$ ) (Equations 8 and 9).

$$D = \frac{12\lambda m}{25\rho c_v} \quad [8]$$

$$D = \frac{6\eta}{5\rho} \quad [9]$$

Equation 5 can be rewritten to give the diffusion mass transport through a spherical surface of radius  $r$  (Equation 10).

$$\frac{dm}{dt} = -4\pi r^2 \frac{dc}{dr} D \quad [10]$$

Equation 10 can be used to determine the mass transport from the liquid/gas interface surrounding a spherical drop of radius  $r_0$  with a concentration of  $c_0$  to a region far from the drop ( $r_\infty$ ) with a vapor concentration  $c_\infty$ . Since  $dm/dt$ , the mass transport, is independent of  $r$ , integration (Equation 11) gives Equation 12. If  $r_\infty$  is very large and if  $c_\infty$  is taken as zero, Equation 15 results.

$$\frac{dm}{dt} \int_{r_0}^{r_\infty} \frac{dr}{r^2} = -4\pi D \int_{c_0}^{c_\infty} dc \quad [11]$$

$$\frac{dm}{dt} = 4\pi D \frac{c_0 - c_\infty}{(1/r_0 - 1/r_\infty)} \quad [12]$$

If  $r_\infty$  is taken as sufficiently large, Equation 12 can be rewritten to give Equation 13. Note that as  $c_4$  approaches  $c_0$  (the air becomes saturated), the rate of evaporation approaches zero.

$$\frac{dm}{dt} = 4\pi D r_0 (c_0 - c_\infty) \quad [13]$$

Equation 13 can be rewritten to give Equation 14

$$\frac{dm}{dt} = \frac{4\pi r_0 D M (p_0 - p_\infty)}{RT} \quad [14]$$

where  $M$  = molecular weight of the vapor, and  $p_0$  and  $p_4$  are the partial pressures of the vapor at the surface of the droplet and at a distance infinitely far from the droplet. In the case of a fire suppressant agent, it can be assumed that  $p_4$  is initially zero, since no agent has yet been released into the room. If  $c_4$  is zero, one obtains Equation

$$\frac{dm}{dt} = 4\pi D r_0 c_0 \quad [15]$$

Equation 15 shows that the transport rate increases with drop size and with the concentration of agent at the liquid/vapor interface.

There are two problems. First, one must determine  $D$  for a real gas (rather than for the hard-sphere idealized gas discussed earlier). Second, and more difficult, one must determine the concentration of agent at the interface.

## 2. Diffusion coefficient

Since measured values of diffusivity are often not available, the only way to obtain values may be to perform estimates based on available equations. Reference 12 lists several correlations for diffusivity; the equation estimated to have the lowest error is the Fuller-Chapman-Giddings equation

$$D = \frac{0.1013T^{1.75} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{0.5}}{P \left[ \left( \sum v_1 \right)^{1/3} + \left( \sum v_2 \right)^{1/3} \right]^2} \quad [16]$$

where  $T$  is the temperature of gases in K,  $M_1$  is the molecular weight of the gas diffusing into the air,  $M_2$  is the molecular weight of the air,  $P$  is the pressure of the gases, and  $v_1$  and  $v_2$  are atomic diffusion volumes which are given in tables. Unfortunately, atomic diffusion volumes are not available for the majority of compounds and must be estimated for many of the compounds of interest.

## 3. Moving Drops

The question of motionless droplets is academic at best. Droplets of fire suppressant chemicals will be rapidly expelled through the nozzle to ensure complete coverage

of the protected area or the fire as well as providing mechanical breakup to smaller droplet sizes. Any realistic evaluation of evaporation must include inertia, gravity, and other forces acting on the droplets. The rapid acceleration of the droplets also distorts the droplets; however, one usually assumes spherical droplets.

The problem quickly escalates from a simple diffusion mechanism to a heat and mass transfer mechanism; it reduces to the calculation of the rate of evaporation or heat transfer from a spherical body in a moving gas stream (in the case of interest, the droplet is in motion within stagnant air, but the mathematics are the same). Solutions to such problems rely on the use of dimensionless numbers such as Reynolds, Nusselt, Prandtl, and Schmidt numbers. The problem is complicated by the fact that flow may be either laminar or turbulent, depending on the value of the Reynolds number; heat and mass transfer are radically different in laminar and turbulent flow.

A simple correction to Equation 13 to allow for the increase in evaporation rate due to motion through air is

$$\frac{dm}{dt} = 4r\pi D(c_o - c_\infty)(1 + \beta Sc^{1/3} Re^{1/2}) = I_o f \quad [17]$$

where  $dm/dt$  equals the evaporation rate with flow around the droplet,  $\exists$  is equal to 0.276 (measured for a sphere),  $Re$  is the Reynolds number characterizing the flow of the air around the drop, and  $Sc$  is the Schmidt number. The term  $f$  is usually called the wind or ventilation factor. It is reported [13] that Equation 17 accurately represents the evaporation rate of droplets in moving air. For very small droplets falling in air,  $f$  is small, approaching 1; for larger droplets in moving streams,  $f$  can be rather large, reflecting the higher heat and mass transfer rates at higher velocity.

SECTION III.  
TECHNOLOGY REVIEW AND ASSESSMENT

A. ELEMENTS

The term “main group elements” is used to denote any element other than transition metals; however, since most work to date has involved organic compounds, particularly halocarbons, such materials are not covered here. Moreover, significant past work under the Next-Generation Fire Suppression Technology Program (NGP) has been performed on amines, ethers, and silicon compounds [14, 15], these compounds are also not included or, in the case of silicon, are only briefly discussed. Phosphorus compounds were examined in the earlier NGP work cited; however, due to the large promise found for such agents, phosphorus compounds are also covered here.

Figure 3 shows a periodic table with the elements considered under the present project in boldface. Note that carbon, oxygen, and the halogens may be (in some cases, are likely to be) present; however, such elements do not form the primary structural features of the compounds considered here. As noted earlier, nitrogen, which was examined in earlier work, is ignored here. Though compounds of helium, neon, and argon are unknown, these are considered in their elemental form. Due to toxicity, the radioactive elements are excluded. Though they are included, the Group I and Group II elements are unlikely to have utility under the project as defined here since most compounds of these are solids.

I	II		III	IV	V	VI	VII	VIII
		H						He
<b>Li</b>	<b>Be</b>		<b>B</b>	C	N	O	F	<b>Ne</b>
<b>Na</b>	<b>Mg</b>		<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	Cl	<b>A</b>
<b>K</b>	<b>Ca</b>		<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	Br	<b>Kr</b>
<b>Rb</b>	<b>Sr</b>	Transition Metals	<b>In</b>	<b>Sn</b>	<b>Sb</b>	<b>Te</b>	I	<b>Xe</b>
<b>Cs</b>	<b>Ba</b>		<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	Po	At	Rn
Fr	Ra							

Figure 3. Elements (in Boldface) Considered Under the Present Project.

## B. COMPOUNDS OF GROUP I ELEMENTS

Group I elements comprise the alkali metals—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). The last element, which is radioactive, is not considered here. Compounds of the alkali metals, in particular potassium and sodium salts, have long been used as fire extinguishing agents. A rather thorough review of the literature on fire extinguishment by compounds of the Group I elements has been prepared [6] and these elements have also been discussed in a report prepared for the USAF [2]. Although these compounds are highly effective extinguishants, the mechanism is still uncertain. Extinguishment may be due to heat absorption, free-radical recombination on particulate surfaces, or homogeneous free-radical removal.

Nearly all compounds of the Group I elements are solids at room temperature, and, therefore, past work has been on either dry chemical powders or solutions. Exceptions are some of the lithium alkyls, which are flammable. Some eutectic mixtures of alkali metal salts have melting points near room temperature; however, the vapor pressures are negligible. Thus, alkali metal compounds must be applied as dry powders or liquid solutions and will not be further considered here. It should be noted, however, that studies have shown that aqueous solutions of some alkali metal compounds are extremely effective fire extinguishants [16].

## C. COMPOUNDS OF GROUP II ELEMENTS

No flame extinguishment data have been found for compounds of beryllium; however, compounds of the other Group II elements (excluding, of course, radium) have been shown to have lower fire extinguishing efficacies than those of the Group I compounds. The absence of beryllium data is likely due to the very high toxicity for beryllium compounds. Like the compounds of the alkali metals, most alkaline earth compounds are solids. Beryllium does, however, form some highly reactive liquid alkyls. Due to their generally unsuitable physical properties, compounds of the Group II elements will not be considered further.

## D. COMPOUNDS OF GROUP III ELEMENTS

### 1. Boron

A number of boron compounds are gases or liquids; however, apparently without exception all are either flammable, highly toxic, or act merely as halon carriers. Thus, both gaseous and liquid boranes (boron hydrides) are known, but all are flammable. Many of the simple halides such as  $\text{BF}_3$ ,  $\text{B}_2\text{Cl}_6$ , etc., are gases or liquids, but these are highly unstable in the presence of moisture and are all highly toxic.

Fire extinguishment testing using standard handheld extinguishers shows that finely divided borax ( $\text{Na}_2\text{B}_4\text{O}_7$ , degree of hydration not specified) is approximately equal to sodium bicarbonate in fire extinguishment effectiveness [17]. The fire suppression capability of this compound may be due to the presence of sodium.

Common flame retardants for fabrics and plastics are sodium borate pentahydrate (borax pentahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ), boric acid [ $\text{B}(\text{OH})_3$ ], boric oxide ( $\text{B}_2\text{O}_3$ ), disodium octaborate tetrahydrate ( $\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$ ), ammonium pentaborate octahydrate [ $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$ ], and zinc borates (e.g.,  $\text{Zn}_4\text{B}_{12}\text{O}_{22} \cdot 7\text{H}_2\text{O}$ ) (Reference 18). In an extensive study of boron compounds, sodium tetrafluoroborate ( $\text{NaBF}_4$ ), a solid, was the most effective single compound for reducing fabric flammability [19]. Note that these flame retardants are all solids.

In this study, no liquid or gaseous boron compounds that have a reasonable toxicity and that are nonflammable have been found. There is no evidence that boron has any catalytic fire suppression capability.

### 2. Aluminum

Aluminum oxide trihydrate ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) is a widely used fire retardant in elastomers [20], where it operates primarily by endothermic release of water to provide cooling. Gaseous aluminum chloride is an effective inhibitor of premixed methane/air flames [21], and the dispersed powder effectively inhibits spark ignition of methane/air mixtures [22]. This activity is probably due to the presence of chlorine rather than to any intrinsic fire extinguishing capability of the aluminum itself. To date, no evidence that aluminum has any catalytic fire

suppression capabilities has been presented. Moreover, the few gaseous or liquid aluminum compounds that exist have serious drawbacks (toxicity, flammability, and/or stability).

### 3. Gallium, Indium, Thallium

No fire extinguishing studies have been reported for the relatively rare elements gallium, indium, or thallium. Toxicity would, moreover, be a serious problem with thallium and indium compounds.

## E. COMPOUNDS OF GROUP IV ELEMENTS

### 1. Carbon

Most potential or known halon replacements for flooding applications are either organic compounds (e.g., the alkyl halides) or have organic substituents. Thus, the presence of carbon is too broad a requirement to be used for a criteria in this report. Most compounds of interest will contain carbon. There is no evidence that carbon imparts any catalytic fire suppression capabilities.

### 2. Silicon

Silicon compounds have been examined in several projects [2, 4, 14, 15]; and there is little or no evidence that silicon offers any inherent fire suppression capabilities. The presence of silicon may, in some cases, offer desirable environmental and toxicological characteristics or physical properties.

### 3. Germanium, Tin, Lead

The only germanium compound studied as a fire extinguishant is germanium tetrachloride,  $\text{GeCl}_4$  [23], whose extinguishing capability may be primarily due to the presence of chlorine. On the other hand, there have been some reports that indicate a possible chemical inhibition for compounds of tin and lead. Thus, lead tetraacetate ( $\text{Pb}(\text{CH}_3\text{COO})_4$ ) and lead acetylacetonate,  $\text{Pb}(\text{CH}_3\text{C}(\text{O})\text{CH}(\text{O})\text{CH}_3)_2$ , neither of which contain halogens, are effective extinguishants [24]. A catalytic mechanism has been proposed for fire extinguishment by tin

[25]. A very recent paper has presented results indicative of a weak catalytic flame suppression action by tin compounds [26].

Despite the scattered indications of catalytic effects for compounds of the heavier Group IV elements, germanium is too costly to be considered, and tin and lead are environmentally unacceptable.

## F. COMPOUNDS OF GROUP V ELEMENTS

### 1. Nitrogen

The chemistry and flame suppression of nitrogen compounds (with an emphasis on fluoroalkyl amines) was discussed in earlier work performed under the Next-Generation Fire Suppression Technology Program (NGP) [14, 15]. One cycle that has been proposed catalyze recombination of hydrogen atoms and hydroxyl free radicals is given in Reactions 1 through 3 [27]. The NO cycle, however, appears to be relatively inefficient [28].



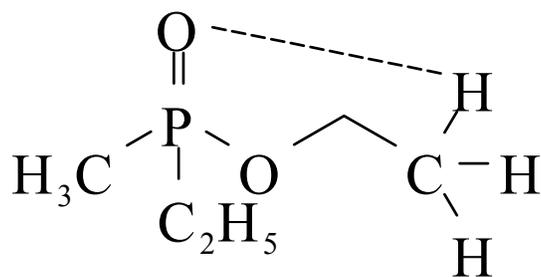
### 2. Phosphorus

A review of the proposed extinguishment mechanisms and testing of phosphorus compounds has been presented [15]. Since the time that the earlier report was being written, a number of new papers and reports have appeared.

A kinetic model has been developed for the combustion chemistry of dimethyl methylphosphonate (DMMP, CCOD ID 1375,  $\text{O}=\text{P}(\text{CH}_3)(\text{OCH}_3)_2$ ) [29]. The opposed-jet burner has been shown to be effective for studying this low-volatility compound [30], and studies with this apparatus have shown that DMMP is a better suppressant when introduced in the oxidizer stream [31] and that DMMP and trimethylphosphate (TMP, CCOD ID 1225,  $\text{O}=\text{P}(\text{CH}_3)_3$ ) are approximately forty times more effective than nitrogen on a per-mole basis in suppressing flames and two to four times more effective than Halon 1301 [32]. Like Halon 1301, the effectiveness is greater when DMMP is introduced on the oxidizer side, rather than the fuel side, of non-

premixed flames even when the amounts actually reaching the flame are taken into account [33]. This behavior is not observed with argon, which has no chemical contribution to flame suppression.

Gas-phase studies in nitrogen show that diethyl methylphosphonate (DEMP,  $\text{O}=\text{P}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)_2$ ) pyrolyzes to form ethene ( $\text{CH}_2=\text{CH}_2$ ), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), and ethyl methylphosphonate ( $\text{O}=\text{P}(\text{OH})(\text{CH}_3)(\text{OCH}_2\text{CH}_3)$ ) [34]. Formation of ethene may result from formation of a six-membered ring transition state (**1**) or by scission of a  $\text{PO}-\text{CH}_2\text{CH}_3$  bond with subsequent loss of a hydrogen atom from the ethyl radical ( $\bullet\text{CH}_2\text{CH}_3$ ). Similar results have been found in pyrolysis studies of diisopropyl methylphosphonate (DIMP), which gives propene ( $\text{CH}_2=\text{CHCH}_3$ ), 2-propanol ( $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ), isopropyl methylphosphonate (IMP,  $\text{O}=\text{P}(\text{OH})(\text{CH}_3)(\text{OCH}(\text{CH}_3)_2)$ ), and methylphosphonic acid (MPA,  $\text{O}=\text{P}(\text{OH})_2(\text{CH}_3)$ ) [35]. A six-membered ring transition state is proposed for formation of 2-propene. Derivatization followed by gas chromatography/mass spectrometry has identified DMMP, methyl methylphosphonate ( $\text{O}=\text{P}(\text{OH})(\text{CH}_3)(\text{OCH}_3)$ ), dimethyl phosphate ( $\text{O}=\text{P}(\text{OH})(\text{OCH}_3)_2$ ), monomethyl phosphate ( $\text{O}=\text{P}(\text{OH})_2(\text{OCH}_3)$ ), MPA, orthophosphoric acid ( $\text{O}=\text{P}(\text{OH})_3$ ), phosphorous acid ( $\text{P}(\text{OCH}_3)_3$ ), and phosphonic acid ( $\text{O}=\text{PH}(\text{OH})_2$ ) as combustion products in a  $\text{CH}_4/\text{O}_2/\text{N}_2$  flame doped with DMMP [36].



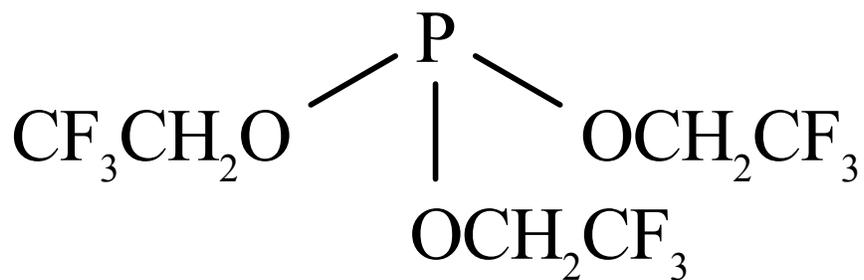
(1)

Based on opposed-flame burner results, there has been significant interest in DMMP as a potential fire extinguishing material. No cup burner values have, however, been determined for DMMP and it would be difficult to obtain such values because of its very high boiling point (181 °C, [37]) and low vapor pressure (1.2 Torr at 25 °C, [38]). Attempts to determine a cup burner extinguishment concentration for a higher volatility nonfluorinated compound, trimethyl phosphite ( $\text{P}(\text{OCH}_3)_3$ ) has also been unsuccessful, due, in this case, to its

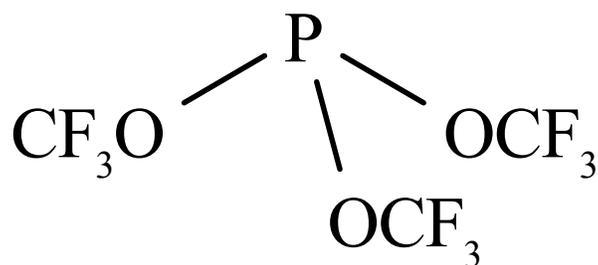
flammability. All of the phosphorus compounds discussed above in this section are, in fact, flammable.

There are two ways around the flammability problem. One is to blend the material with a nonflammable carrier; the other is to work with fluorinated alkyl derivatives of phosphorus. Cup burner testing using both of these approaches has been carried out and the results are presented in this report.

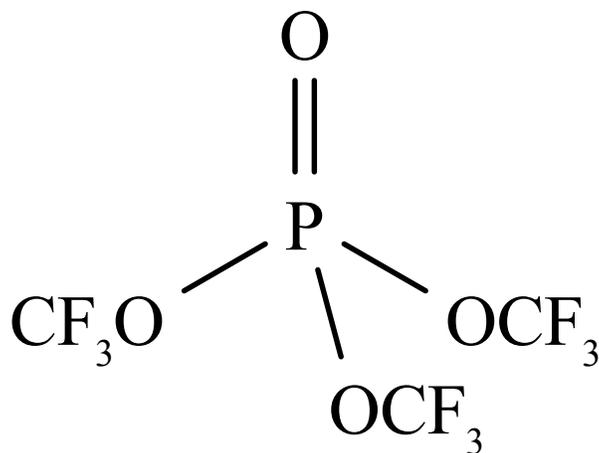
Previous work has shown that the compound tris(2,2,2-trifluoroethyl)phosphite (2), TFEP, CCOD ID 1236, exhibits a particularly low cup-burner extinguishment concentration [15]. (More recent and careful work, performed under the present project, gave an extinguishing concentrations of 1.77, 1.81, 1.81, 1.79, and 1.69 vol% (average:  $1.78 \pm 0.04$  vol%) for *n*-heptane fuel.) This compound, however, has a relatively high boiling point of 130 to 131 °C at 743 Torr pressure [39]. One might, therefore, consider tris(trifluoromethyl)phosphite (3) or tris(trifluoromethyl)phosphate (4), CCOD ID 1348, as promising materials.



(2)



(3)



(4)

Tris(trifluoromethyl)phosphite ( $\text{P}(\text{OCF}_3)_3$ ) has not been reported; however, tris(trifluoromethyl)phosphate ( $\text{O}=\text{P}(\text{OCF}_3)_3$ ) has been prepared by oxidation of tris(trifluoromethyl)phosphine ( $\text{P}(\text{CF}_3)_3$ , CCOD 1351, [40]). The phosphate has a boiling point of 52 °C at 760 Torr pressure and a melting point of -86 °C. The vapor pressure  $p$  in Torr can be fit to the equation  $\log_{10}p = -1445/T + 7.33$ , where  $T$  is in units of K, corresponding to a Trouton's Constant of 85.22 J/mol-K. This equation gives a calculated vapor pressure of 304 Torr at 25 °C.

One might consider whether tris(trifluoromethyl)phosphite could be prepared by reaction of trifluorophosphine ( $\text{PF}_3$ ) with carbonyl fluoride ( $\text{O}=\text{CF}_2$ , CCOD ID 696) (Reaction 4). The enthalpy of reaction ( $\Delta H_r$ ) for Reaction 4 was estimated based on bond energies from values in References 41, 42, and 43. Table 4 gives the data used in the calculation. The column marked "Basis" indicates the type of compound or types of compounds used to determine the bond energy.  $\Delta H_r$  is estimated as 92 kJ/mol (22 kcal/mole). Thus, the reaction is slightly endothermic, and the reverse reaction may provide a pathway for decomposition. This is particularly likely since the entropy of the decomposition reaction would almost certainly be positive due to the increase in the number of moles of gas.



Were the material to be formed as the phosphonate structure,  $\text{O}=\text{P}(\text{CF}_3)(\text{OCF}_3)_2$ , the reaction is less endothermic, with  $\Delta H_r$  estimated as to be 58 kJ/mol (14 kcal/mole). Again, however, the reverse reaction should have a positive entropy change. Even though the reactions

are predicted to be endothermic, one must recognize that the use of average bond energies is highly suspect.

TABLE 4. ENTHALPY OF REACTION FOR  $\text{PF}_3 + 3 \text{O}=\text{CF}_2 \rightarrow \text{P}(\text{OCF}_3)_3$ .

Bond				$\Delta H$ , Total for Bond Formation or Dissociation
Type	Number	Energy, kJ/mol (kcal/mol)	Basis	kJ/mol (kcal/mol)
Reactants				
P-F	3	498 (119)	$\text{PF}_3$	1495 (357)
C-F	6	490 (117)	$\text{CF}_4$	2939 (702)
C=O	3	749 (179)	ketones	2248 (537)
			Sum	6682 (1596)
Product, Phosphite Structure				
P-O	3	368 (88)	$\text{P}_4\text{O}_6$	1105 (264)
C-F	9	490 (117)	$\text{CF}_4$	4410 (1053)
C-O	3	358 (85.6)	organics	1075 (257)
			Sum	6590 (1574)
Product, Phosphonate Structure				
P-O	2	368 (88)	$\text{P}_4\text{O}_6$	736 (176)
P=O	1	456 (109)	$\text{O}=\text{PCl}_3$	456 (109)
P-C	1	306 (73)		306 (73)
C-F	9	490 (117)	$\text{CF}_4$	4410 (1053)
C-O	2	358 (85.6)	organics	716 (171)
			Sum	6624 (1582)

### 3. Arsenic, Bismuth, Antimony

Antimony has been extensively used in flame retardants, usually in conjunction with bromine-containing compounds. This work has been reviewed [2] and the information presented earlier will not be repeated here. No studies on fires suppression by arsenic or bismuth

compounds has been found. Compounds of arsenic and antimony are too toxic to be considered as fire extinguishing compounds.

## G. COMPOUNDS OF GROUP VI ELEMENTS

### 1. Oxygen

Oxygen compounds are included under other headings and will not, therefore, be covered here. There is no indication that oxygen compounds have any type of catalytic fire suppression capability.

### 2. Sulfur

A sulfur dioxide cycle (Reactions 5 and 6) has been proposed to inhibit combustion by removal of hydrogen atoms [28].



Perfluoroalkyl sulfur compounds (Table 5) are of some interest due to their relatively high stability toward oxidation and hydrolysis. Bis(trifluoromethyl)sulfide ( $\text{CF}_3\text{-S-CF}_3$ , CCOD ID 1362) can be prepared by heating commercially available bis(trifluoromethyl)disulfide ( $\text{CF}_3\text{-SS-CF}_3$ , CCOD ID 1363) at 425 to 435 °C for 3 to 4 days [44]. This and other perfluoroalkylsulfides can also be prepared by heating or photolysis of  $\text{R}_f\text{OC(O)R}_f$ , where  $\text{R}_f$  is a perfluoroalkyl group [45, 46]. The ester starting materials are prepared by reaction of  $\text{R}_f\text{-S-Cl}$  with silver perfluorocarboxylates ( $\text{AgOOCR}_f$ ). The derivatives  $\text{R}_f\text{-SF}_2\text{-R}_f$  can be prepared by fluorination of the corresponding sulfide with  $\text{ClF}$  or  $\text{F}_2$ , and from these, hydrolysis gives  $\text{R}_f\text{-S(O)-R}_f$  [47, 48]. A number of these materials are remarkably stable toward both hydrolysis and oxidation [44, 46, 47].

Table 5. Perfluoroalkyl Sulfur Compounds.

CCOD ID	Compound	Formula	Boiling Point, °C
1362	1,1,1,3,3,3-hexafluoro-2-thiopropene	CF <sub>3</sub> -S-CF <sub>3</sub>	<sup>a</sup> -22.
1282	1,1,1,3,3,4,4,4-octafluoro-2-thiobutane	CF <sub>3</sub> -S-CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 6.3
1364	1,1,1,3,3,4,4,5,5,5-decafluoro-2-thiopentane	CF <sub>3</sub> -S-CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 38.6
1365	1,1,1,2,2,3,3,3-octafluoro-2-thiopropene	CF <sub>3</sub> SF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 21.0
1366	1,1,1,2,2,3,3,4,4,4-decafluoro-2-thiobutane	CF <sub>3</sub> SF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 44.1
1367	1,1,1,2,2,3,3,4,4,5,5,5-dodecafluoro-2-thiopentane	CF <sub>3</sub> SF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 69.3
1368	1,1,1,2,2,3,3,4,4,5,5,6,6,6-dodecafluoro-3-thiopentane	CF <sub>3</sub> CF <sub>2</sub> SF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 69.5
1369	1,1,1,3,3,3-hexafluoro-2-oxo-2-thiopropene	CF <sub>3</sub> S(O)CF <sub>3</sub>	<sup>b</sup> 37.3
1370	1,1,1,3,3,4,4,4-octafluoro-2-oxo-2-thiobutane	CF <sub>3</sub> S(O)CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 58.2
1371	1,1,1,3,3,4,4,5,5,5-decafluoro-2-oxo-2-thiopentane	CF <sub>3</sub> S(O)CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 64.0

<sup>a</sup>Reference 44.

3

<sup>b</sup>Reference 46.

One major drawback of sulfur compounds is the formation of toxic sulfur oxides during fire extinguishment.

### 3. Selenium, Tellurium

The only compound containing one of these elements for which fire extinguishment capabilities have been reported is perfluoroselenolane [49]. There is no indication that selenium or tellurium compounds exhibit catalytic flame inhibition or that such compounds would have particular utility as halon replacements. Toxicity would be of some concern.

## H. GROUP VIII ELEMENTS

Of the non-radioactive Group VIII elements, the noble gases (helium, neon, argon, krypton, and xenon), only xenon and to a much lesser extent, krypton are known to form compounds. These compounds are strong oxidizing agents and would probably act to increase flame intensity rather than decrease it. On the other hand, no studies of xenon or krypton compounds in flames has been carried out. Like nitrogen, all of the noble gases exhibit fire extinguishment capabilities by dilution and cooling.

## SECTION IV. CUP BURNER

### A. OVERVIEW

In anticipation of future work on halon replacements, a number of modifications were made in the NMERI cup burner. These are described below.

### B. AIR FLOW

#### 1. Mass Flow Controller

A change was made in the cup burner to allow the use of a mass flow controller for the air flow for all ranges. In the past, this method has been used only for the largest air flows. The air flow rates are obtained from a Cole-Parmer Model 33116-60 mass flow controller, which covers flow rates from 0 to 50 Standard Liters/Minute (SLM) calibrated for air against a NIST standard. (This instrument is used to monitor the air flow rate regardless of the method used to determine agent concentration.) Here SLM is defined as 760 torr and 70 °F (21.11 °C). From 0 to 50 °C and up to 150 psia (50 psia back pressure) the outputs are independent of temperature and pressure. The readings, R in SLM, can be converted directly to air molar flow rates,  $n_A$ , without concern about the actual operating conditions (Equation 18). In this equation, 22.41408807 is the conversion from liters to moles for a temperature of 273.15K and a pressure of 760 Torr. The molar flow rates can, of course, be converted to volumetric flow rates in any part of the air stream if the pressure and temperature are known.

$$n_A = R(273.15/21.11+273.15)/22.41408807 \quad (18)$$

Factory calibration gives the data shown in Table 6 and Figure 4. With a forced intercept of zero, the data are fit well with a line  $\text{actual} = 0.9928 * \text{measured}$ .

TABLE 6. ACTUAL VERSUS MASS FLOW METER READING FOR AIR FLOW RATES.

Reading, L/min	Actual Measured, L/min	Difference, percent
0.000	0.000	0
12.678	12.597	+0.6
25.359	25.052	+1.2
38.000	37.748	+0.7
50.244	49.922	+0.6

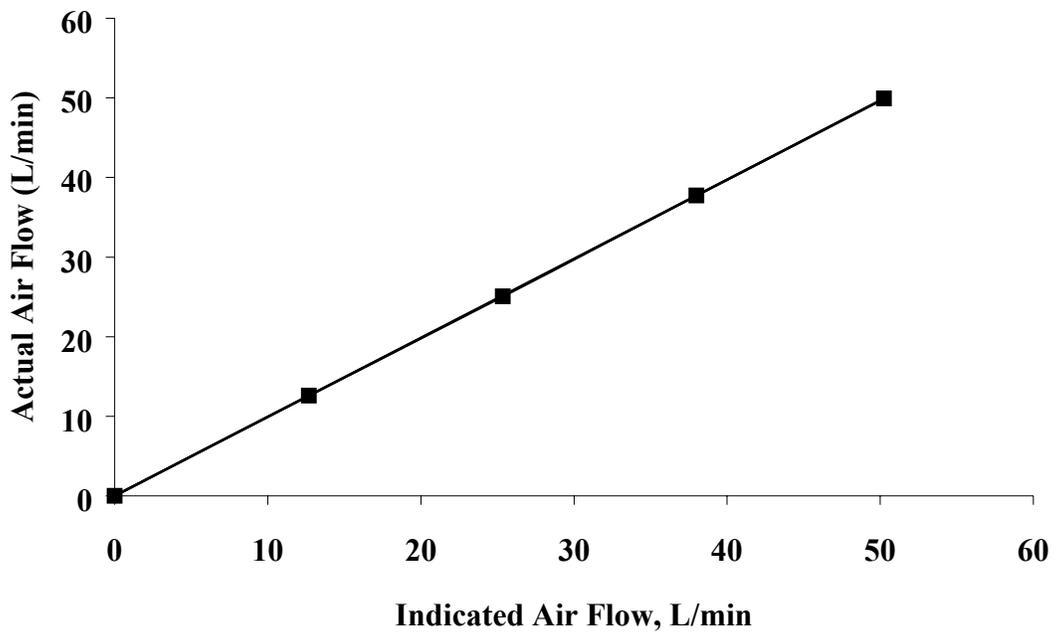


Figure 4. Actual versus Mass Flow Meter Reading for Air Flow Rates.

## 2. Digital Bubble Meter

Since the change to a mass flow controller for the NMERI Standard Cup Burner was made during the present project, not all air-flow data were collected using the flow controller. In some cases, a bubble meter with an electronic digital readout was used. The

digital bubble meter used is a Humonics, Inc. digital flowmeter (a bubble meter with a digital electronic readout), Serial Number 006528. The digital flow meter is calibrated at 23 °C and 1025 mb (768.8 Torr) against a National Institute of Standards and Technology (NIST) calibrated standard TN 244763 Teledyne HBM-1A #1265. The calibration showed percent errors of -1.61, +1.61, and -0.40 percent at flow rates of 1.34, 6.53, and 12.74 L/min.

### C. AGENT FLOW

A number of techniques have been used by various researchers in the past to determine agent flow. We discuss these below and indicate those used here.

#### 1. Oxygen Monitoring

The draft ISO standard for cup burner testing [50] suggests calculating the extinguishment concentration,  $C$ , from the cup burner chimney oxygen concentration,  $O_2$ , and the supply air oxygen concentration,  $O_2(\text{sup})$  (Equation 19).

$$C = 100*[1-O_2/O_2(\text{sup})] \quad (19)$$

There are two major problems with this method: (1) Measurement of oxygen concentrations is usually relatively imprecise. For example, the oxygen analyzer used by one organization performing cup-burner determinations, is claimed to have a measurement accuracy of 0.15 vol% [51]. Since the concentration of oxygen in air is approximately 20 vol%, this corresponds to an accuracy of 0.75 percent for the oxygen concentration. Because two oxygen concentrations are required, the ratio of  $O_2/O_2(\text{sup})$  has an accuracy of only 1.5 percent. (2) For halocarbon agents, the calculation of the agent concentration,  $C$ , requires subtraction of two numbers with nearly the same value — 1 and the  $O_2/O_2(\text{sup})$  ratio, which is nearly 1 — to give a small number (around 0.05). For example, for FC-3-1-10 (*n*-perfluorobutane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$ ) which has an extinguishment concentration of approximately 5.3 vol% with *n*-heptane fuel [52], the  $O_2/O_2(\text{sup})$  ratio would be approximately 0.947. Thus, an error of 1.5 percent means that the ratio could vary from 0.933 to 0.961 with a calculated agent concentration (Equation 1) varying from 3.9 to 6.7 vol%, a possible error of  $\pm 24$  percent for a cup burner value of 5.3 vol%. Thus, the oxygen concentration method, which is relatively precise for inert gas extinguishants, which

have very large extinguishing concentrations, is virtually worthless for halocarbon agents. It is recognized, of course, that this method may have a greater utility for inert gas agents.

Minor problems with the oxygen concentration method is that there are concerns about the effect of temperature and pressure on the oxygen concentration values and the requirement for removal of a portion of the air/agent stream below the cup during extinguishment if continuous measurements are required. In fact, most continuous analytical methods require disturbance of the agent/air flow.

## 2. Direct Measurement of Extinguishment Concentration

Gas chromatography, spectroscopy, and other methods (e.g., measurements based on thermal conductivity) have been used to determine the actual concentration of agent in the chimney following extinguishment. These methods are attractive since they measure the actual agent concentration; however, they are often less precise, labor intensive, and provide sources for error in manipulation of samples. For GC work, known concentrations of agent obtained by dilution of a standard are used for calibrations. Following extinguishment, the air and agent flow rates are maintained and aliquots are removed with a gas-tight syringe and injected into a gas chromatograph. Peak areas are used to determine concentrations. Past experience with GC analyses show that periodic recalibration is needed and that, at best, such analyses are accurate to within no better than 5 percent.

## 3. Mass Flow Rate

We have developed a computerized system that monitors the weight of a small cylinder from which agent is delivered as a function of time and calculates continuously updated flow rates. An electronic scale with an RS-232 output is connected to a computerized data acquisition. The mass flow rates,  $m_a$ , permit the direct calculation of the agent molar flow rates,  $n_a$ , without concern about temperature or back pressure (Equation 20).

$$n_a = m_a/MW \quad (20)$$

From the molar flow rates of the agent (Equation 20) and the air, the agent concentration,  $C$ , can be directly calculated (Equation 21). If the mass flow controller is used to determine the air flow rate (Equation 18), no part of this calculation requires any knowledge of

the temperature or pressure (or back pressure) within the system as long as ideality can be assumed (nonideality can, of course, be taken into account), the temperature at the mass flow controller is between 0 and 50 °C, the air pressure is less than 150 psia, and the back pressure is less than 50 psia. (At no time do the temperatures and pressures come close to the limits. The back pressures are always well under 1 psia, and the temperatures at the flow meter are around 25 °C.)

$$C = n_a / n_A + n_a \quad (21)$$

The following gives an error analysis for the mass flow rate method. A typical mass flow rate for FC-3-1-10 (*n*-perfluorobutane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$ ) to extinguish a *n*-heptane flame in the NMERI Standard Cup Burner operating with an air flow rate of 10 L/min is approximately 0.094 g/sec, which can be measured with the electronic balance coupled to the data acquisition system to  $\pm 0.001$  g/sec. Since the electronic balance output is almost perfectly linear over small mass changes, the precision is the same as the accuracy. Note that this does not require the assumption that the absolute mass measured is exact, only that the mass differential is exact. Thus, the accuracy of the agent mass flow rates is approximately 1.0 percent independent of any pressures, temperatures, or back pressures. Combining the predicted accuracies for the air and agent mass flow rates gives an accuracy of approximately 2 percent for the extinguishment concentration for a *n*-heptane flame using FC-3-1-10 employing Equation 21). Very similar results are obtained for other halocarbon/fuel combinations. Note that this precision is an order of magnitude better than that possible for an oxygen analyzer. It is also better than the precisions estimated for gas chromatographic, FTIR, and rotametric methods, all of which require calibration for the specific agents used and, in most cases, knowledge of temperatures, pressures, and/or back pressures.

#### 4. Digital Bubble Meter

In some cases, the flow rates of some of the less efficient highly gaseous agents were determined using the Humonics, Inc. digital flowmeter described earlier. The accuracy of this meter is approximately 2 percent for agents with extinguishing concentrations of 10 vol% in the NMERI Standard Cup Burner with an air flow rate of 10 L/min and the accuracy increases as the agent efficiency decreases (more agent required).

#### D. CUP BURNER TESTING OF BLENDS CONTAINING PHOSPHORUS COMPOUNDS

Trimethylphosphite, which is more volatile than DMMP, was blended with both HFC-227ea and HFC-125 and the extinguishment concentrations were determined using the NEMRI Standard Cup Burner, a digital bubble meter for air flow, and mass flow rate for the agent. The results (Table 7) show a reduction of 1 to 2 percent (absolute) in the extinguishment concentration compared to the pure carriers.

TABLE 7. CUP BURNER EXTINGUISHMENT CONCENTRATIONS, *N*-HEPTANE FUEL.

Compound	Formula	Test Number	Extinguishment Concentration, vol% (Determinations)
HFC-227ea	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	981209-2	6.25 ± 0.03 (6)
Trimethylphosphite/HFC-227ea (7.2%/92.8%)	P(OCH <sub>3</sub> ) <sub>3</sub> /CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	981209-1	5.31 ± 0.15 (6)
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	981208-1	8.75 ± 0.21 (6)
Trimethylphosphite/HFC-125 (12.2%/87.8%)	P(OCH <sub>3</sub> ) <sub>3</sub> /CHF <sub>2</sub> CF <sub>3</sub>	981209-4	6.79 ± 0.15 (5)

## SECTION V. SAPPHIRE EXPERIMENTS

### A. SAPPHIRE 0-7 WITH DIMETHYLMETHYLPHSOPHONATE (DMMP).

#### 1. Apparatus

The Sapphire 0-7 burner (Figure 5) was designed for the study of low volatility flame inhibition agents. Compounds are introduced from a heated cell, and the entire burner is wrapped with Nichrome resistance wire and heated to prevent condensation of the agent in the burner. The burner allows infrared spectroscopy of post-combustion gases. Openings are provided near the top of the borosilicate glass “chimney” (about 8.7 in [22 cm] above the surface of the burner). A Fourier Transform Infrared (FTIR) Spectrophotometer with external optics can be located so that the optical axis passes through the post-combustion gases. A wire mesh screen placed over the top of the “chimney” prevents external air currents from disturbing the test environment; IR-transparent windows in the openings in the borosilicate glass “chimney” are not required. Very satisfactory data have been obtained with this very simple arrangement. The Sapphire 0-7 burner also allows optical absorption photometry of the pre-combustion gases.

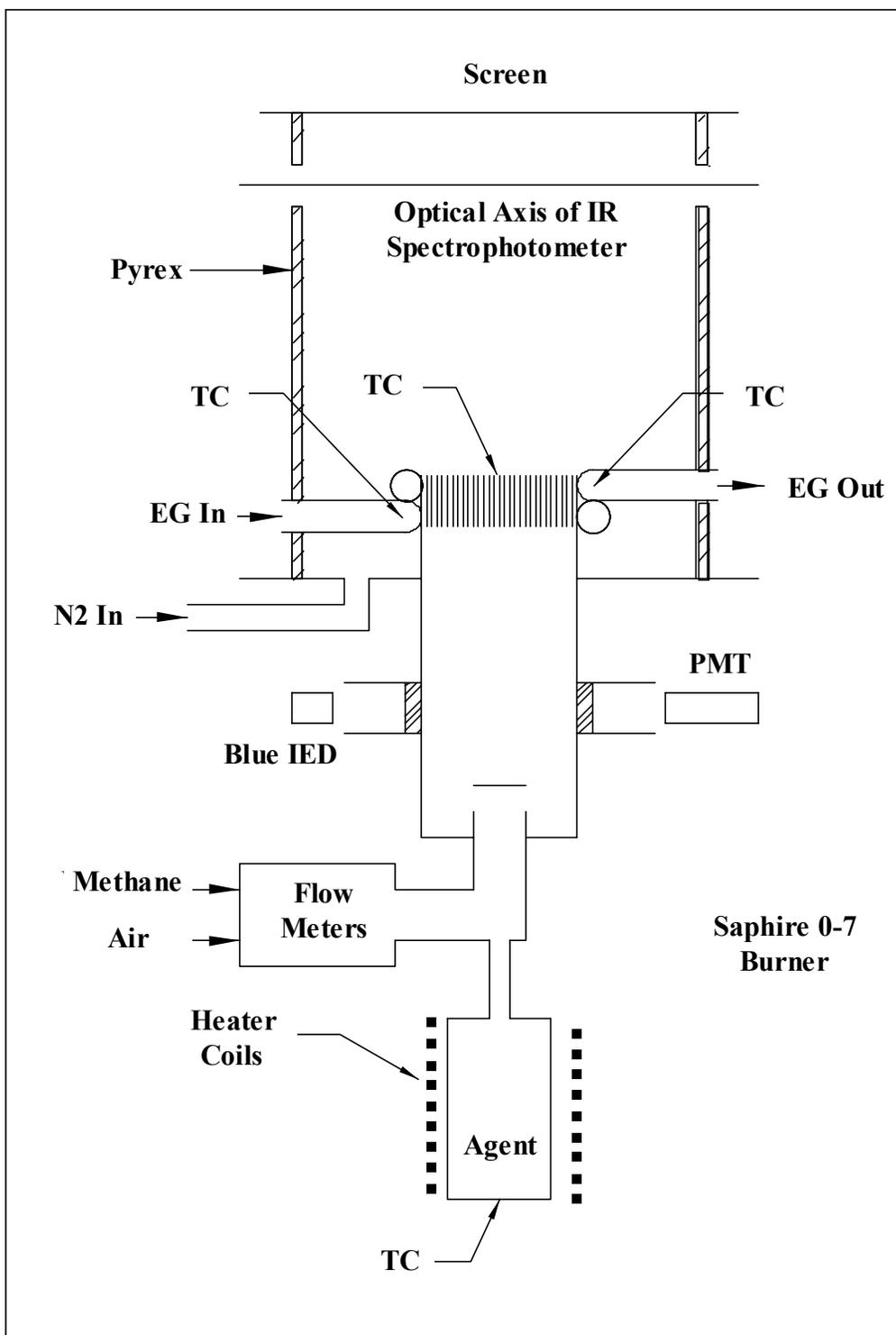


Figure 5. The Sapphire 0-7 Atmospheric-Pressure Burner.

## 2. Objective

The objective of these experiments is to characterize the extinguishment of atmospheric-pressure methane-air flames by dimethyl methylphosphonate (DMMP,  $\text{O}=\text{P}(\text{CH}_3)(\text{OCH}_3)_2$ ). These experiments should not only provide a baseline for subatmospheric experiments with the Sapphire 2 apparatus, but also provide insights into the mechanism of inhibition and extinguishment of flames by this compound. In these experiments, inhibition of the premixed methane-air flame is studied as a function of the mole fraction of inhibiting agent added to the premixed gases. Both the flow rate of methane and flow rate of air are fixed, and the amount of extinguishing agent is varied. Two air streams are used; one stream passes through a bubbler containing the extinguishing agent, while the other stream bypasses the bubbler. The concentration of extinguishing agent introduced into the flame is controlled by controlling the relative flow rates of the two air streams.

## 3. Experiment DMMP\_A

A stoichiometric flame,  $\Phi = 1.00$ , was used in this experiment, and the bubbler was thermostated at room temperature. Although information regarding the vapor pressure of DMMP has been sought in the available literature, no information has been found as of this writing. Accordingly, it was assumed that the vapor pressure is 20.3 torr, and all calculations were based on this value. The heat extracted by the burner was measured as a function of the flow rate of DMMP. Approximately 35 percent of the inhibition curve was obtained; the flame was not extinguished. The maximum degree of inhibition was achieved when the entire air flow was passed through the bubbler. To obtain a greater degree of inhibition, it will be necessary to use another technique for introducing the DMMP into the premixed gases. Except for the three data points at the highest flow rate of air through the bubbler, the data points fell on a straight line. This is the behavior characteristic of a thermal (physical) agent. At this point, there is no obvious evidence of a contribution by a catalytic extinguishment mechanism. It is suspected that the three data points that did not lie on the straight line (and were above the line), were the result of partial saturation of the air stream with DMMP at these very high flow rates. The estimated mole fraction of DMMP at extinguishment (obtained by extrapolation to the x axis) was 0.057

(5.7 vol%). Note that, if a smaller vapor pressure had been assumed for the DMMP, the mole fraction at extinguishment would have been proportionately smaller.

#### 4. Experiment DMMP\_B.

Experiment DMMP\_B was a repeat of DMMP\_A. This was an atmospheric pressure experiment with  $\Phi = 1.0$ . Midway through Experiment DMMP\_A, there had been a jump in the data; although we believed that we knew how to treat the data for DMMP\_A, a confirmatory experiment was desirable. Experiment DMMP\_B did confirm the results of the prior experiment. There was a fortuitous difference between the two experiments. While Experiment DMMP\_A was run with a DMMP reservoir temperature of 23 C, the reservoir temperature in Experiment DMMP\_B was 19 C. The slopes of the delta-q lines were likewise different; the slopes were 1.71 cal/unit and 1.41 cal/unit for the 23 C and 19 C experiments, respectively. Making the assumptions that (1) the slope of the line is proportional to the extinguishment effectiveness, and (2) that the extinguishment effectiveness is proportional to the vapor pressure of the DMMP in the bubbler, we can estimate the heat of vaporization of DMMP from these data. The value obtained (using the Clausius-Clapeyron relationship) is 35 kJ/mol. For comparison, one obtains a value of 36 kJ/mol using Trouton's Rule, taking Trouton's Focus to be 88 J/mol-K and a boiling point of 181 C. The splendid agreement is far too good, given the small difference in temperature; however, it gives one considerable confidence in the validity of the experimental configuration. With this heat of vaporization as a starting point, it can then be estimated that the vapor pressure of DMMP at 19 C is 3.83 torr. Assuming complete saturation of the air stream in the bubbler over the linear region of the data, it can then be estimated that the mole fraction at extinguishment is 0.063 (6.3% by volume). This is similar to the value expected for this compound. In summary, the Sapphire 0 experiments are yielding excellent data of considerable value. In addition to providing estimated extinguishment concentrations, these experiments also give insight into the extinguishment mechanism. At this point, it can be said that the data are consistent with a purely thermal mechanism. Experiment DMMP\_C was performed on 29 Oct; for this experiment,  $\Phi = 0.9$ . At first look, it looks like something may have happened part way through the experiment which invalidated the data; analysis will continue today.

## SECTION VI. RESULTS AND CONCLUSIONS

### A. RESULTS

With few exceptions, compounds of the s block elements (the alkali metals and alkaline earths—Groups IA and IIA) are solids and do not meet a primary requirement for materials considered here (that the compounds be gases or liquids). Most of the compounds which have halogens (Group VIIB) as a primary constituents and which could be considered as halon replacements are either halocarbons, amines, or ethers (which are excluded) or contain other non-carbon main group elements and are considered with those elements. The only non-halogen, non-transition metal elements that appear to provide any significant catalytic fire suppression capabilities are the alkali metals, tin, lead, and phosphorus.

### H. IMPORTANT FINDINGS AND CONCLUSIONS

With one major exception, the results of the search have been disappointing. Few materials based on main group elements with potentially acceptable physical (primarily, volatility) and toxicological properties have been identified. The lowest molecular weight materials (i.e., the materials with the highest volatilities) often have hydrogen or halogen atoms directly attached to non-carbon atoms. The former (containing hydrogen) are often flammable, and the latter (containing halogens) are usually toxic (owing to hydrolysis). Both often have low stabilities. Moreover, few elements provide catalytic fire suppression capabilities, and compounds of most of those do not meet the requirements of this study. A major exception is fluoroalkyl phosphorus compounds, which hold significant promise despite their relatively low volatility.

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