The Cup Burner as a Suppression Mechanism Research Tool: Results, Interpretations, and Implications

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An understanding of the issues in identifying non-ozone depleting **fire** extinguishants as replacements for halons requires knowledge of fire extinguishment processes. This invited paper is intended as a limited review and in part, a simplified overview tutorial, to provide background for the discussion of mechanisms of suppression, a key theme at the HOTWC'97 meeting. This paper is not meant to be a comprehensive treatment nor to go into detailed chemical or physical processes. The contents are borrowed freely from our earlier output, including presentations at previous Halon Alternatives Technical Working Conference meetings in Albuquerque.[1] They include the contributions of current and former coworkers at the Naval Research Laboratory. Reference 2 extends the discussion of our halon substitute program *to* intermediate and full scale evaluations.

Suppression Mechanisms

The existence of a fire depends on sufficient availability of fuel, oxidizer (usually oxygen), energy (heat), and the key flame radicals. Fires can be suppressed by the removal of any of these which can occur by a number of mechanisms, usually in concert. The extinguishment pathways listed in Table 1 serve as a convenient framework for discussion.

TABLE 1
EXTINGUISHMENT PATHWAYS

Physical - Nonreactive		Chemical - Reactive
Energy	Spatial	
Heat Capacity	Dilution	Scavenging
Thermal Conductivity	Separation	Catalytic
Decomposition	Decoupling	(Third-body Effects)

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A flame can normally exist only between two temperature limits. The adiabatic flame temperature is the highest temperature to which the reaction exoergicity can heat the product gases. The minimum propagation temperature is the lowest temperature that will allow sufficiently rapid chemical reactions to maintain the flame. When energy sinks such as heat capacity or thermal conductivity lower the flame zone temperature below the minimum propagation temperature (approximately 1600 K for organic fuels), reaction rates slow and extinguishment results. Decomposition also requires energy input **to** break bonds. This reaction mode, but not including inhibiting reactions of the decomposition products, is usually considered a physical process.

Dilution slows reaction rates by the law of mass action. An agent present at 10 percent means dilution of reactants by 10 percent. Bimolecular reaction rates are then slowed to **81** percent of their former rate. Separation is the classical concept of physical separation of fuel from oxidizer. A blanket or foam layer are examples. Decreasing energy feedback to unburned fuel reduces fuel vaporization and decomposition. Examples of decoupling of the energy and radical rich zone from the unburned gases are blowing out a candle or blasting out an oil well fire. Separation and decoupling mechanisms are not usually significant in total flooding applications.

Chemical inhibition pathways are very efficient and are the primary reason for employing the bromine containing halons. The radical species responsible for flame propagation are directly removed from supporting combustion by establishing alternative reaction paths. **A** suppressant that removes one radical (or a defined number of radicals) acts as a radical scavenger. **A** species that can remove more than one radical may be functioning as a catalyst, having a much greater suppressant impact. HBr, formed by bromine radical combining with a hydrogen atom, can react with a second hydrogen atom to form a much less reactive hydrogen molecule, regenerating the bromine radical to repeat its chemical suppression action. Facilitating chemical reactions by acting as a third-body is not as significant. Such interaction could be called physical since there are no chemical changes involved.

The molecular reaction

$$H + O_2 \rightarrow OH + O - 16.8 \text{kcal/mole} \qquad (1)$$
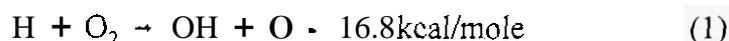
is usually the major oxygen consumption and primary branching reaction. It is key in flame propagation as one reactive radical generates two reactive radicals. If its rate is decreased sufficiently, the fire will be extinguished. Dilution (lowering reactant concentrations), energy removal (reducing temperature) and radical removal (chemical scavenging or catalytic reaction) all take place with chemical suppression agents. Any suppressant, by virtue of its mass, possesses physical action. Chemical pathways to various degrees can also be operative.

Our experimental research indicated a model based on heat capacity could be used to predict physical action extinction requirements. To get a better appreciation of the relative contributions of heat capacity, thermal conductivity, and dilution, we (primarily Dr. Doren Indritz[3]) computer modeled atmospheric pressure hydrogen-oxygen-nitrogen combustion using 11 species, 58 reactions, thermodynamic values, temperature dependent rate reactions, and heat and mass

transfer for each species. The flammability limit as a function of composition was mapped out and matched experimental values quite well.

We then studied suppression of stoichiometric hydrogen-air mixtures by adding varying amounts of physical agent. By selectively 'turning off' the program subroutines that calculated the heat capacity, thermal diffusion, or dilution effects, we quantified their contribution to achieving flame extinction. Helium effectiveness is due primarily to dilution (50%) and thermal conductivity (30%), with heat capacity effects accounting for only 20 percent. For diatomic nitrogen, heat capacity contributes 50 percent, followed by dilution and thermal conductivity contributions. For polyatomic species, such as CF_4 and SF_6, heat capacity is the dominant extinguishment factor, contributing over 70 percent of the suppression effectiveness.

Experimental
Laboratory scale fires used a liquid pool diffusion flame burner patterned after the Imperial Chemical Industries and Factory Mutual Research Corporation cup burners. The burner consists of a **2.8** cm diameter tapered Pyrex cup in a chimney of 10.5 cm id. Air and agents are mixed and flow up past the liquid fuel fire. Experiments with n-heptane fuel were used for model development, although other fuels, such as 2-propanol, gave similar results.

Agents tested in the 1970s included He, Ne, Ar, N_2, CO_2, CF,, SF_6, CF_3Cl, CF_3Br, CF,I, SF_5Cl, SF_5Br, and S_2F_{10}. Many more chemicals have subsequently been tested. An experiment consisted of igniting the liquid fuel in flowing air, allowing flame stabilization, and adding agent until the diffusion flame was extinguished. Gas samples were taken from the inlet line and analyzed for agent concentration.

Modeling
The basis for separating out the physical and chemical components was Huggett's observation[s] that atmospheres with a heat capacity above a certain (wide) range would not allow combustion. The NRL n-heptane cup burner study allowed quantifying that 'range' to a single number. We observed that the calculated extinguishing mixture heat capacity when normalized per mole of oxygen was approximately constant for the physically acting agents'. Normalizing per mole of oxygen in the gas mixture is valid because the heat of combustion for most hydrocarbon fuels (and many organics) is approximately constant per mole of oxygen consumed. **A** more rigorous treatment uses **AH,** the normalized enthalpy of heating. This is the heat capacity as a function of temperature integrated from room temperature up to the minimum propagation temperature of 1600 K, given in equation (2).

$$\Delta H' = \Sigma_i \frac{X_i}{X_{O_2}} \int_{298}^{1600} C_{pi}^T \, dT \qquad (2)$$

where $\mathbf{AH'}$ = Mixture Enthalpy of beating per mole O_2
        X_i = Mole fraction of component I in the mixture.
        C_{pi}^T = Heat capacity of component I at temperature T.
        X_{O_2} = Mole fraction of oxygen in the mixture.

The agent percentages required to extinguish the heptane pool fires and the energy abstracted by agent heat capacity integrated from room temperature to 1600 K are given in Table **2.**

TABLE **2**
Agent Concentration (%) Required to Extinguish n-Heptane Cup Burner Diffusion Flames
and Energy Abstracted by Heat Capacity

Agent	% to Extinguish	Enthalpy Abstracted
Ar	**41**	**58** kcal/(mole O_2)
Ne	**37**	**56**
He	**32**	**52**
N_2	**30**	**58**
CO_2	**21**	**58**
CF_4	**16**	**64**
SF_6	**11**	**63**
CF_3Cl	**6.9**	**48**
CF_3Br	**3.1**	**42**
CF_3I	**3.2**	**42**
SF_5Cl	**13**	**70**
SF_5Br	**4.2**	**47**
S_2F_{10}	**10.5**	**82**

Equation **(2)** can be inverted. The mole fraction of new agent **A**, $X(A)$, required to extinguish an air pool fire, can be calculated from its enthalpy of heating $\int C_{PA} \, dT$.

$$X(A) = \frac{AH(0.21) - 7.9}{\int C_{PA} \, dT + AH(0.21) - 7.9} \qquad (3)$$

The value **7.9** is the enthalpy of heating for nitrogen; **0.21** is the oxygen mole fraction in air. This formalism ignores dilution and thermal conductivity effects. However, any changes between agents are minimized by the large nitrogen concentration in air. Table **2** shows the **A H** values for the polyatomics CF, and SF_6 to be approximately **64** kcal / (mole O_2). This value will be used for prediction calculations for polyatomic molecules. Please see Reference **6** for a more complete treatment of our linear physical and chemical model development.

We define a suppression fraction X^s as the mole fraction of agent used experimentally divided by $X(A)$, the mole fraction of that agent required (or predicted) to cause extinguishment.

$$X^s = X(\text{experimental})/X(A) \qquad (4)$$

The extinction index, the sum of individual agent suppression fractions (analogous to the flammability index), is equal to unity at extinguishment.

$$\Sigma_i X_i^s = 1 \quad \text{(at extinguishment)} \tag{5}$$

The linear additivity of physical action (Eq. (5)) was proven by extinguishment experiments with CF, and SF_6 mixtures. This then constitutes our physical action suppressant predictive model.

Water requirements for fire extinction can be predicted by including the latent heat of vaporization in the calculation. Optimum performance would occur if vaporization occurred exclusively in the flame sheet. The minimum amount of water required is the same volume as liquid Halon 1301, or 2/3 the mass. Less than half the energy abstraction is due to vaporization. The water molecule has a relatively high heat capacity per weight as it has a high number of bonds per molecular mass. Generation and transport into the flame of sufficient fluid above its gas phase equilibrium vapor pressure (i.e., in mixed gas and liquid form) is the key issue.

Chemical Model
Being able *to* calculate the physical suppression contribution of agents is necessary for evaluating the presence and extent of chemical action. For a first order chemical effectiveness calculation, we assume physical and chemical effects are additive. This assumption lets us separate the suppression fraction, X^s, into physical, X^{sp}, and chemical, X^{sc} terms for each species.

$$X^s = X^{sp} + X^{sc} \tag{6}$$

The suppressant series CF_3Cl, CF_3Br, CF_3I, and SF_5Cl and SF_5Br are of special interest. The SF_5X compounds are model analogs to the CF_3X compounds. S_2F_{10} is of interest as it decomposes into two SF_5 radicals. Using a value of 64 kcal / (mole O_2) in **Eq. (3)** for AH', we calculate the amount of CF_3Y and SF_5Y agents required for physical suppression. Equations (4), (5), and *(6)* then allow calculation of X^{sc}, the chemical suppression fraction.

This simple chemical model rationalizes that since the bond strengths $D(CF_3\text{-}F)$ and $D(SF_5\text{-}F)$ are much greater than any $D(CF_3\text{-}X)$ or $D(SF_5\text{-}X)$ (X = Cl, Br, I), one can assume that initially the C-Cl, C-Br, S-Cl and S-Br bonds are broken while C-F and S-F bonds remain intact. It is not important to the model whether the initial suppressant molecule reaction is an abstraction or dissociation. X^{sc}, the chemical suppressant fraction for agent AB, can be separated into $X^{sc}(A)$ and $X^{sc}(B)$.

Suppression fraction normalized by species mole fraction is called "Suppressant Factor" F^s as:

$$F^s(A) = X^s(A)/X_A \tag{7}$$

The extinction index (equation (6)) at extinguishment can be generalized as a linear sum as

$$\Sigma_i X_i F^{sp}(I) + \Sigma_i X_i F^{sc}(I) = 1 \tag{8}$$

where: $F^{sp}(I)$, $F^{sc}(I)$ = Suppressant Factor, Physical and Chemical, respectively.

When the sum of agent mole fraction times suppressant factor reaches an extinction index value of one, extinguishment occurs. Although linear additivity may not always be true since different radicals may act via different "bottlenecks," this approximation will be used for this model.

Solving equation (8) using the data on the chemical agent **series** as linear equations, we find[6] suppressant factor values **as** listed in Table 3. Values **less** than zero imply the species acts as a flame promoter rather than **as** a suppressant.

The SF_5 radical (negative suppressant factor) is a flame promoter rather than an inhibitor. The CF_3 and I radicals are chemical suppressants, with the I radical as powerful as the Br radical. Halon 1301 (CF_3Br) suppression action is 20% physical, 25% chemical due to CF, and 55% chemical due to Br. This linear physical and chemical predictive model is applicable to fuel - air systems.

TABLE 3
SUPPRESSANT FACTOR VALUES

Physical		Chemical	
	F^{sp}		F^{sc}
CF_4, CF_3Cl, CF_3Br, CF_3I	6	CF_3	7
SF_6, SF_5Cl, SF_5Br	**9**	SF_5	-3
S_2F_{10}	15	Cl	1.6
		Br	18
		I	17

The above model assumes complete chemical interaction. It is simple to use and is instructive. However, this assumption is not completely valid. A ligand on an agent molecule may be strongly bound. In that case, the physical predictive model should be valid. If the bond is very weak, or the ligand very reactive, the combined physical and chemical model should be valid. Reality is frequently in the middle ground. The actual suppressant agent concentration required for extinguishment will be bounded by the respective predictions of the above two models. The degree to which chemical action comes into play can be weighted by the likelihood, under flame conditions, of unimolecular decomposition or abstraction reaction. Development of this modified chemical predictive model continues, including incorporation **of** the flame promoting effects of carbon-carbon bonds and hydrogen and carbon atoms, and a factor for propensity for bond rupture. Agent requirements are typically predicted correct to better than 10% (relative) (7).

Nonlinear empirical chemical action
We know the linear additivity assumption made above is not completely valid. We saw that mixtures of physical agents with halon 1301, primarily a chemical agent, show an enhanced efficiency deviation from linearity. Figure 1 plots the suppression fractions F^s (Eq. 7) for mixtures of SF_6 and Halon 1301, CF_3Br. There *is* a large domain of suppression enhancement. Extinguishment occurs at **an** extinction index **(Eq.** 8) as low as 0.81, less than a value of 1.0.

This enhancement is <u>not</u> synergism, but rather a manifestation of non-linearity. This can be better understood by reploting the same data showing the suppression fractions for physical and

chemical pathways in Figure 2. The actual chemical fraction, unity minus the physical fraction, is shown as greater than the linear model calculated chemical fraction. The ratio of these two functions is shown as the relative efficiency of CF_3Br chemical suppression as a function of CF_3Br concentration. This work was the first demonstration quantitatively showing the variation of chemical suppression efficiency as a function of concentration.

Suppressant action can be divided into: Physical, no chemistry; Chemical - Scavenging, reacting with a set number of flame radicals (e.g., $F + H = HF$); and Chemical - Catalytic, reacting with flame radicals via a catalytic cycle (e.g., $Br + H = HBr$, $HBr + H = Br + H_2$) and thus potentially removing a large number of species required for flame propagation. A physical mechanism produces linear, but inefficient suppression effectiveness, while catalytic reactions involving bromine and iodine containing suppressants produce high chemical effectiveness. This enhanced effectiveness decreases at higher agent concentration as the chemical catalytic effect saturates.

Free oxygen model

Fire extinction is achieved with a linear model calculated suppression fraction sum of less than 1. A different formalism is now required. The physical model is based on a suppressant adding at least 26 kcal / (mole O_2) energy sink from enthalpy of heating in air systems. A more general equivalent criteria is to evaluate the amount of oxygen "canceled out" by the suppressant. This is done by our Free Oxygen model adapted from work by Tucker *et al.*[8]

$$\text{FREE } O_2 = [O_2] - \Sigma_i \left([O_2]_{ext}/[X_i]_{ext}\right) [X_i] \qquad (9)$$

where $[O_2]$ and $[X_i]$ are mixture oxygen and agent concentrations

$[O_2]_{ext}$ and $[X_i]_{ext}$ are oxygen and agent concentrations at extinguishment, either from experiment or model (physical)

When the calculated concentration of oxygen "canceled out" by all suppressant agents present equals the experimental oxygen concentration, the mixture will not support combustion. Model validity is shown by considering the following two mixtures (all in volume per cent): O_2 19.7, N_2 80.8 and O_2 26.9, N_2 50.8, SF_6 21.2. While oxygen concentrations are very different (about 20% and 27%) calculated Free Oxygen values are 5.37 and 5.40 %, and Halon 1301 concentrations required for extinguishment are 2.00 and 2.03 %, respectively. Halon 1301 effectiveness is a function of Free Oxygen, increasing significantly at low values.'

Extinguishment is a function of Free Oxygen, not actual oxygen, concentration. Argon is a very different agent, by itself or in blends. It must reduce oxygen concentration to just above 12% to extinguish a n-heptane cup burner fire. Sulfur hexafluoride will extinguish the same fire at just under 19% oxygen. The Free Oxygen empirical model can predict suppressant concentration requirements in agent mixtures and blends, including as a function of oxygen concentration. The additional suppressant required to protect against reflash in a post extinguishment, carbon dioxide rich and oxygen depleted environment can also be predicted.

The effectiveness of Halon 1301, determined as a function of Free Oxygen in the gas mixture to which it is added, is shown in Figure 3. The suppression index is an absolute, not relative, figure of merit. A suppression index of **4**, for example, means four percent oxygen concentration is neutralized by one percent agent.

Discussion
The nonlinear empirical chemical model can be used to differentiate and characterize chemical suppression activity, Chemical catalytic action is manifested by nonlinear behavior; physical action by a constant suppression index. The absolute magnitudes are also different. There is no longer a limitation to air systems. Depleted **or** enriched oxygen atmosphere suppression requirements can also be predicted. Another important feature of this nonlinear empirical chemical model is that once initial extinction data have been determined, the model can be used to predict agent requirements for mixtures and blends. Halon replacements can be designed to take advantage of 'enhancement' effects, while minimizing ODP and toxicity concerns.

Air contains approximately **7** % Free Oxygen. The rest of the oxygen is "neutralized" by the need to heat the nitrogen up to a minimum flame propagation temperature. Slight decreases in oxygen, from only 21 % to 19 %, represent an approximate decrease in free oxygen from **7** % to 5 Y_0. Knowing the oxygen (and other major component gases) concentration in a fire extinction test is crucial. The minimum agent concentration **required** to extinguish a fire in air can be **40** % above the agent requirement determined in 19 Y_0 oxygen. Test results can only be validly compared if under similar Free Oxygen values, **or** if adjustments are calculated.

Summary
Several different fire extinction models have been generated for predicting agent concentrations required for extinguishing fires. They are not exclusive and can serve different purposes. The modified linear physical and chemical model can predict agent concentrations for fires in air with only an approximation of agent heat capacity. The nonlinear chemical model requires one experimental data set, but can then predict concentration requirements for agent blends and for varying oxygen concentrations. Experimental results are required to form the data basis for model prediction. Further development of **our** flammability computer modeling with more agent chemistry should minimize that requirement, where adequate kinetic data are available. The important lesson is to interrelate model and real world fire extinguishment. To correctly evaluate agent performance, in real scale testing one must **know** the O_2 and other major gas concentrations at the fire in addition to the agent concentration. Failure to account for O_2 depletion and O_2 concentration at the fire during extinguishment will result in an erroneously high agent performance evaluation.

Models such as described above are needed to understand fire suppression mechanisms. Appreciation of these mechanisms is needed to help design laboratory experiments properly relevant to real world fires. Care must be taken to determine the importance of the additional factors that come into play in large scale fire extinguishment.

Acknowledgments

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MIXTURE EFFECT
CF$_3$Br - SF$_6$ EXTINGUISHMENT

SF$_6$
CF$_3$Br
SUM

SF6 SUPPRESSION FRACTION

SUPPRESSION FRACTION
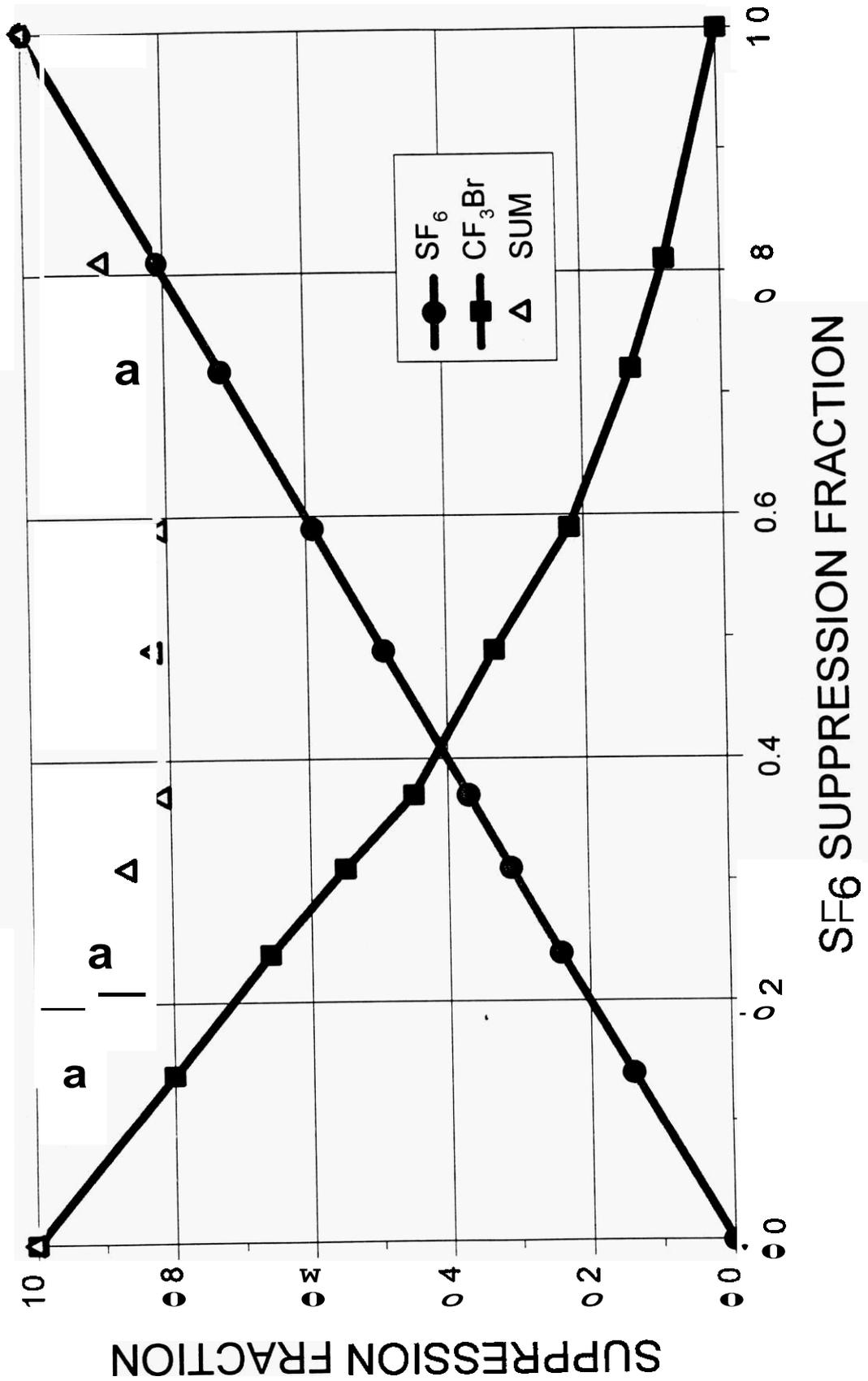
Figure 1: Suppression Fraction Summation from Halon 1301 and SF$_6$ Extinguishing Mixtures

CHEMICAL SUPPRESSION EFFICIENCY
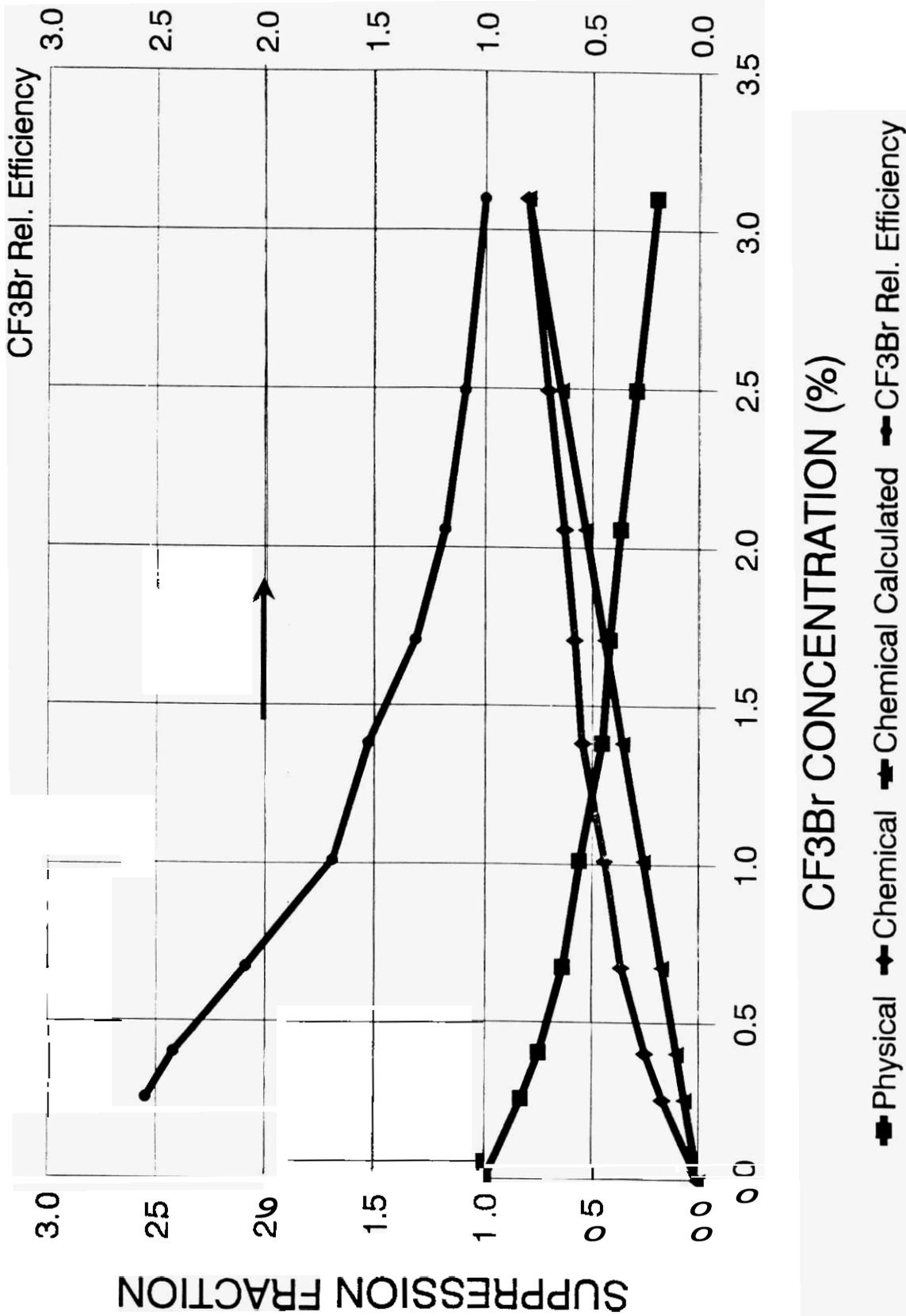
Figure 2

Chemical and Physical Components of Suppression Fraction from Halon 1301 and SF_6 Extinguishing Mixtures, and Relative Chemical Efficiency of Halon 1301 as a Function of Concentration

CF3Br

AIR/O2/N2/SF6 SUPPRESSION MIXTURES

■ AIR/O2/N2 MIXTURES   ▲ AIR/O2/SF6 MIXTURES
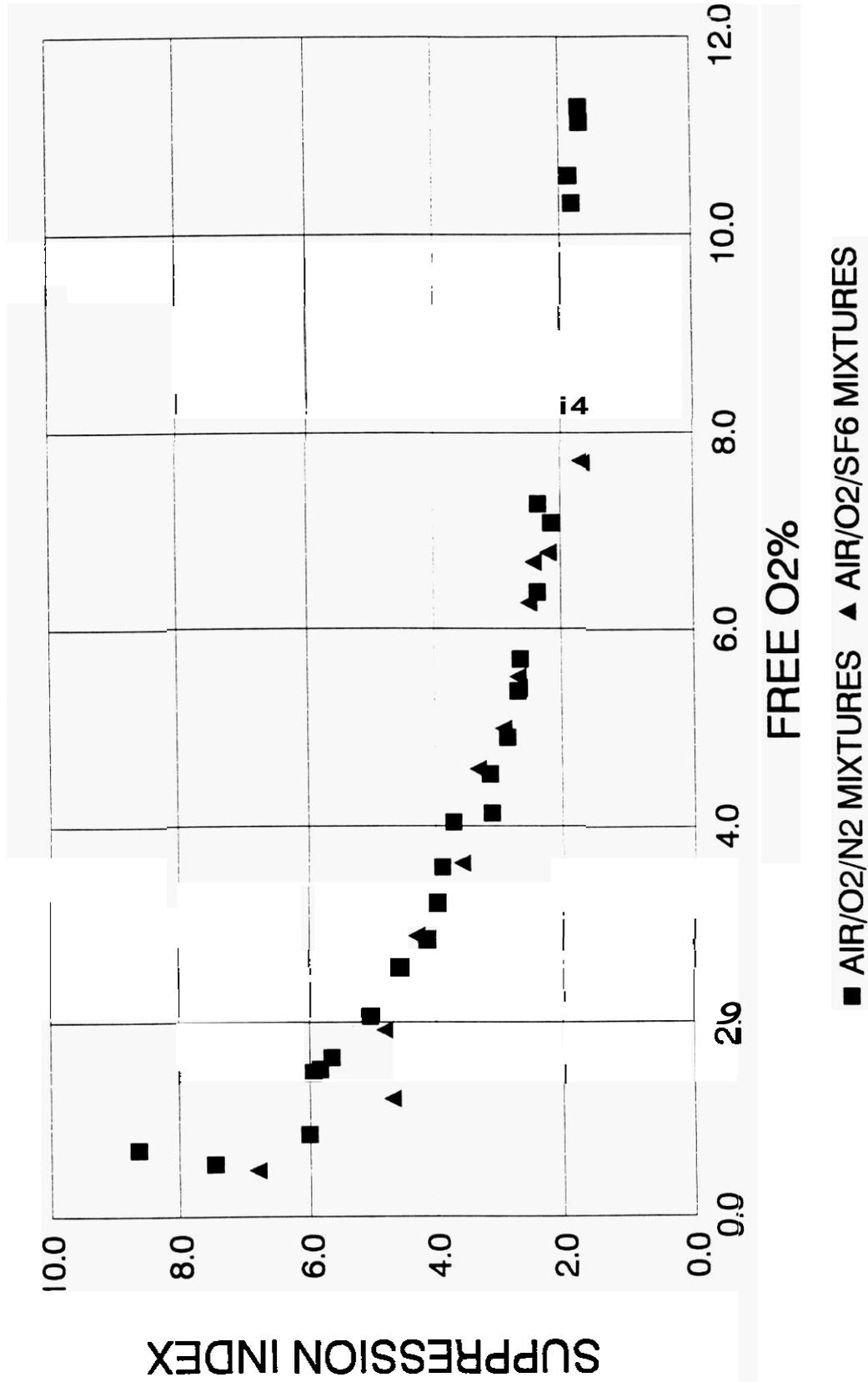
Figure 3: Halon 1301 Suppression Index as a Function of Free Oxygen