

CHARACTERIZATION OF EXTINGUISHANTS BY HEAT EXTRACTION FROM FLAMES

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INTRODUCTION

Unfortunately, the best understood extinguishant, Halon 1301, must over time be replaced. Accordingly, a program has been established to explore the chemistry of alternate extinguishants, with the expectation that this knowledge will facilitate selection and/or design of replacement agents.

Flame velocity is a measure of the progress toward extinguishment of inhibited flames. In an early and enduring paper, Botha and Spalding determined the adiabatic flame speed by relating the observed flame speed to the amount of heat removed by the burner as the mixture ratio was changed; a nearly linear relationship was found.' It follows that it should be possible to relate the observed heat removed by the burner to the progress toward extinguishment of inhibited flames. Based on this idea, it was decided to measure the heat extracted by the burner as a function of the amount of extinguishant added. This report details the information that can be gained from this type of experiment.

At the outset, one might expect three different types of behavior.

(1) Physical Extinguishment. In the case of a physical extinguishing agent, the amount of energy absorbed by the agent (and hence not available to be extracted by the burner) should depend only on the heat capacity of agent, and one would expect an inverse linear relationship between the amount of heat extracted by the burner and the amount of agent added to the flame.

(2) Chemical Extinguishment. In the case of a chemical agent in which each molecule of agent is "used" just once, one would again anticipate an inverse linear relationship; the slope of the line should, of course, depend both on the heat capacity of the agent and on the specific chemistry in which the agent is involved.

(3) **Catalytic Chemical Extinguishment** If, however, the agent is involved in a catalytic extinguishment process, a more complex relationship might be expected; Halon 1301, CF_3Br , is a classic case in point. When only a small amount of agent is present, each catalytic radical is involved in a large number of cycles; however, as the amount of agent is increased, the catalytic radicals begin to encounter competition for the dwindling number of target species (H atoms, in the case of Halon 1301), and the agent becomes less and less effective on a per molecule basis. As a consequence, one should expect some sort of non-linear relationship between energy absorbed by the burner and amount of agent added.

EXPERIMENTAL

A laboratory Meker burner (diameter = 3.7 cm) was modified for these experiments. To facilitate heat transfer, the flame-holding grid was silver soldered to the inside of the burner rim. The heat absorbed by the burner was carried off by ethylene glycol, circulated at a measured flow rate by a gear pump through a cooling loop (3/16" copper tubing) silver soldered to the outside of the burner rim. The increase in the temperature of the ethylene glycol was measured by a pair of thermocouples, located in the cooling loop just below the points of attachment of the loop to the burner rim. The individual gases were metered through calibrated flow meters, mixed, and introduced into the bottom of the burner through a diffuser, which assured uniformity of the flame across the surface of the burner. A chromel-alumel thermocouple was spot welded to the surface of the grid in the center of the burner. Cylinder gases (oxygen, C_2H_2 methane, argon, and extinguishant) were used as received.

In a typical experiment, the total flow rate in the uninhibited flame was 3700 cc/min (@ 0.83 atm). The mole fractions of Ar, O_2 , and CH_4 were 0.76, 0.15, and 0.09, respectively; $\phi = 1.17$ for this flame. With the flow rates of diluent, oxidizer, and fuel held constant, the amount of extinguishant was increased incrementally, and the temperature increase of the ethylene glycol in the cooling loop was measured after a suitable delay (about 6 minutes) for thermal equilibration. Typical temperature differences were 10°C for uninhibited flames.

RESULTS

General.

Figure 1 illustrates a typical result. Several comments are in order. First, the

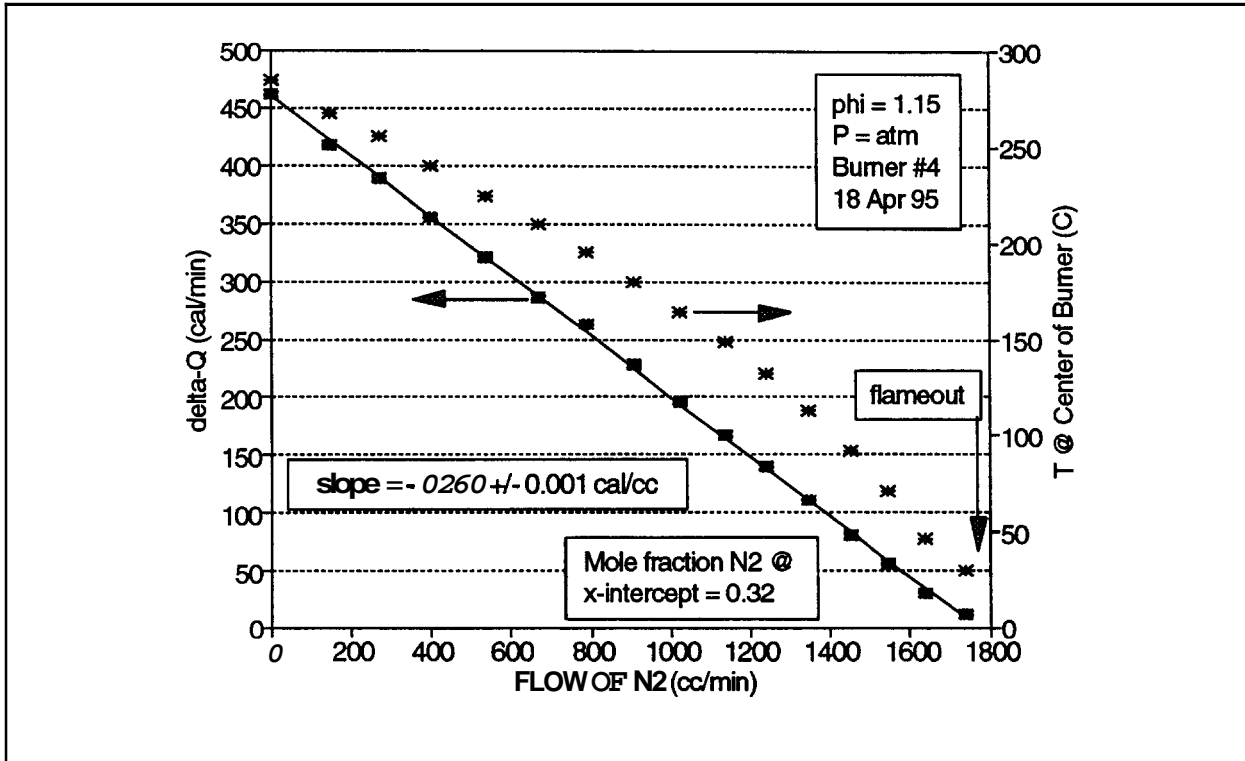


Figure 1. Quenching by Nitrogen

heat extracted by the burner from an uninhibited flame (no extinguishant added) is a strong function of the fuel/oxidant ratio; for ease of comparison of various experiments, it is important to use the same fuel/oxidant ratio as a starting point for each experiment. Second, the heat extracted from the flame by the burner is burner dependent; thus, data such as the slope of the curve obtained for a particular agent can be strictly compared only against the data for another agent using the same burner. However, the point of extinguishment appears to be *independent* of the burner used, and thus permits comparison against data from other workers. Third, the experiment illustrated by Figure 1 was conducted in an ambient air atmosphere, with provisions to prevent disturbance by air currents, but with no provisions to prevent entrainment of air into the flame. Note that flameout occurred at the point that is predicted by extension of the line to the point at which no heat was transferred to the

burner from the flame. This result is characteristic of uninhibited flames with $\phi = 1.17$. However, for significantly richer flames or flames in which the extinguishant serves as a fuel as well as an extinguishant, a different result is observed; *vide infra*. Fourth, the temperature measured at the center of the grid is also an excellent predictor of extinguishment; as expected, this temperature is very near room temperature at extinguishment.

Physical Extinguishants.

Table 1 lists results of individual experiments for six agents which are believed to inhibit and extinguish flames solely by a physical mechanism, namely, the absorption of heat due to the heat capacity of the extinguishing agent.

TABLE 1. DATA FOR PHYSICAL EXTINGUISHING AGENTS

AGENT	ϕ	SLOPE (cal/cc)	x-INTERCEPT (mole fraction)	C_p @ 25°C (cal/mol-°C)	Calculated Δt (°C)
He	1.17	0.151 ± 0.002	0.44	4.97	883
Ar	1.17	0.271 ± 0.004	0.73	4.97	1,585
N ₂	1.15	0.260 ± 0.001	0.32	6.96	1,030
CO ₂	1.17	0.268 ± 0.004	0.20	8.87	712
CF ₄	1.17	0.501 ± 0.012	0.14	14.59	732
C ₄ F ₁₀	1.10	2.33 ± 0.03	0.054	45.7	ca 850

The last column in Table 1 indicates the temperature to which the agent would have to be heated by the flame in order to absorb the amount of heat that is *nut* carried away by the ethylene glycol. As an example, consider the results displayed in Figure 1 for nitrogen. The slope of this line is -0.260 cal/cc, or 7560 cal/mol. Using published enthalpy data in the JANAF Tables: the final nitrogen temperature is found to be 1030°C. Needless to say, this conceptually simple framework somewhat oversimplifies the situation; a detailed analysis would also consider the thermal conductivity of the agent and the change of heat capacity of the product gases of combustion as the agent is added. However, this framework was adopted because of its considerable utility in a system in which other parameters are held constant. Examination of the data in the last column reveals that the calculated temperatures

are quit reasonable. The origin of the unexpectedly high value for argon is still being studied, but most likely is related to the fact that argon is the diluent used in all of these experiments.

Physical Extinguishants in Rich Flames.

A typical result for a rich flame is illustrated by Figure 2. Except for the fuel/oxygen ratio and different burner, this experiment was essentially identical to that illustrated by Figure 1. However, note the departure from straight-line behavior for nitrogen flow rates greater than 1200 cc/min. The additional heat carried off by the burner at these high flow rates can be attributed to the combustion of the excess

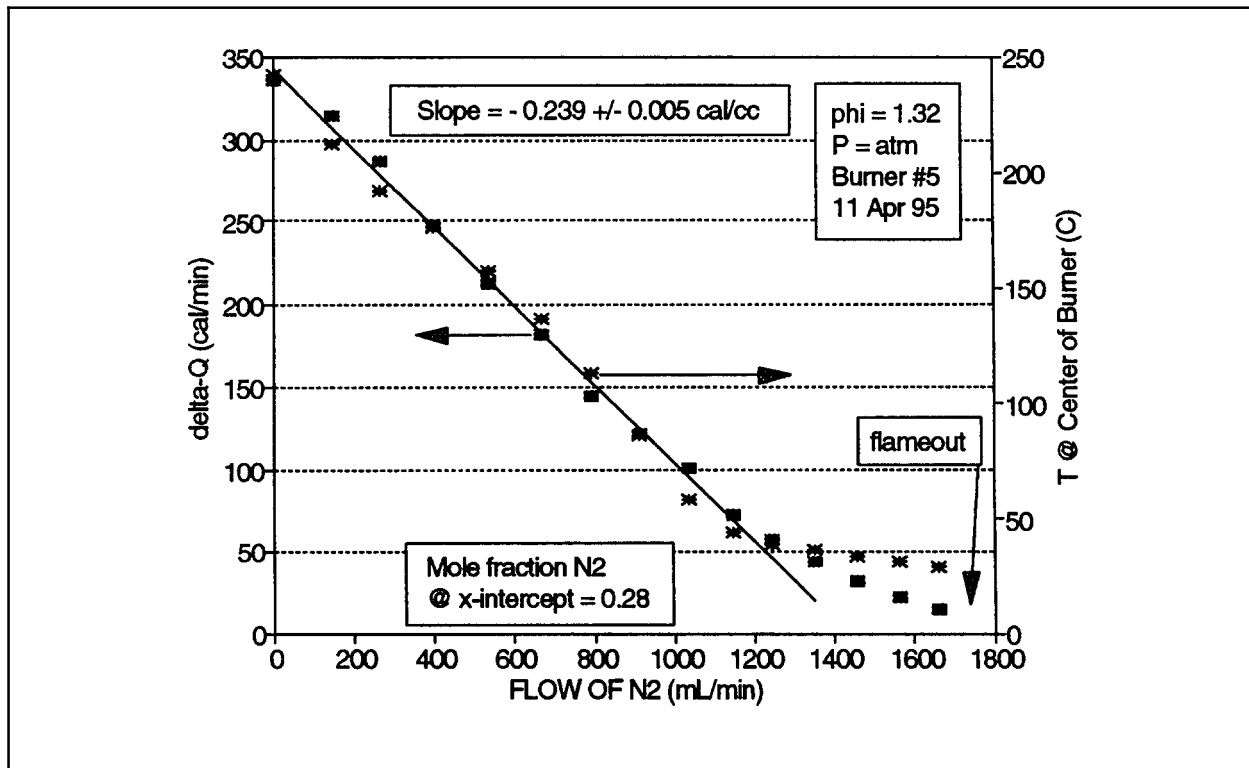


Figure 2. Quenching of a Rich Flame by Nitrogen

methane with entrained oxygen from the ambient air environment. This hypothesis is supported by the observation that the flame remained attached around the rim of the burner until flameout was finally observed at about 1700 cc/min, although the flame lifted off from the center of the burner (as evidenced by the temperature at the center of the burner) at about the 1200-cc/min point .

Catalytic Extinguishants.

The experiment with CH_3Br , illustrated by Figure 3, yielded a dramatically different result. While, the heat capacity of methyl bromide contributes significantly to the extinguishment of the flame, the characteristic linear relationship typical of a physical extinguishing agent is absent, and the data points in this figure are best fitted using an equation of the form $y = a + b \exp(-cx)$. The remarkable effectiveness of CH_3Br as an extinguishing agent is evidenced by the initial slope of this curve. If one were to use the initial slope to calculate a temperature for the CH_3Br , assuming that this molecule was solely a physical extinguishant, one would obtain the absurd value

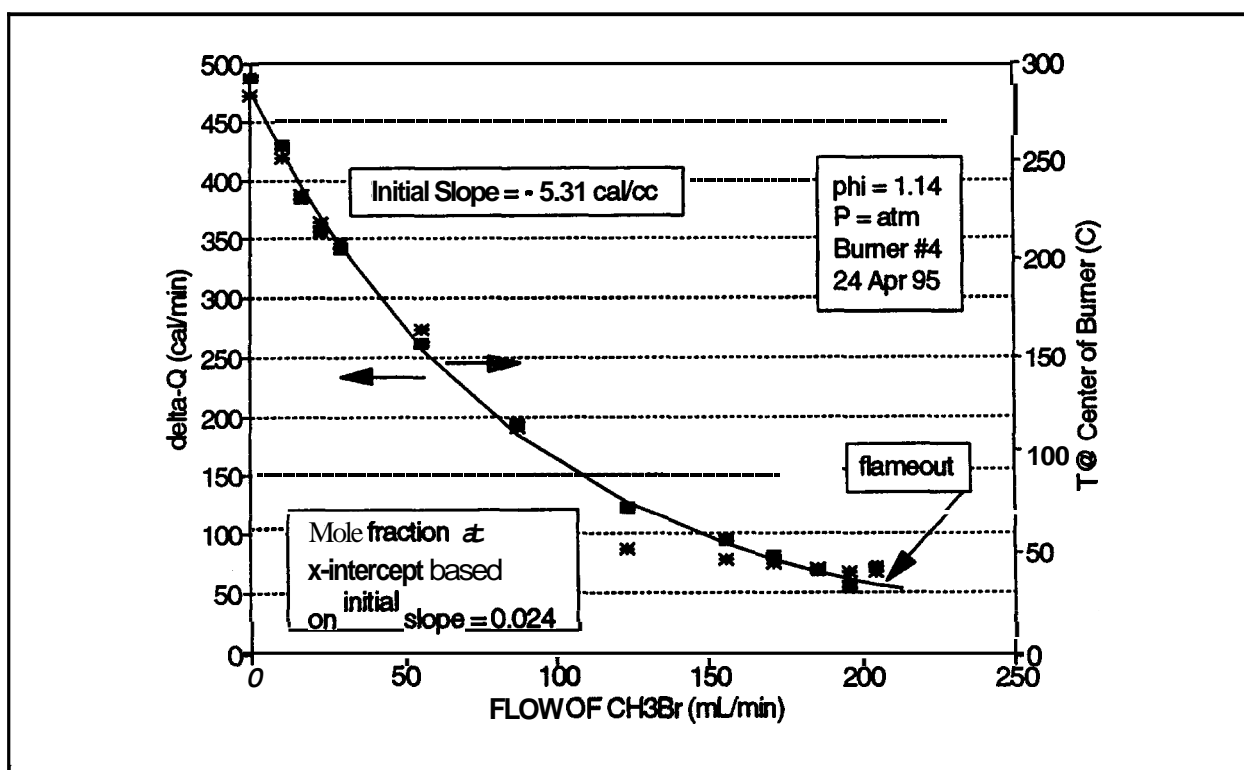


Figure 3. Quenching by CH_3Br

of about 5900°C . On the other hand, the slope at the point of flameout is -0.47 cal/cc , a value consistent with the conclusion that the dominant mechanism at this point is physical. Between these two extremes, the importance of the catalytic chemical process steadily diminishes as the amount of CH_3Br is increased, as suggested earlier in this paper.

Table 2 summarizes the data for experiments with five agents. The results for

CF₃Br and CF₃I are qualitatively identical to those for CH₃Br. In each of these cases, the slope reported in Table 2 is the initial slope at the intercept of the curve with the y-axis.

TABLE 2. DATA FOR CHEMICAL EXTINGUISHING AGENTS

AGENT	ϕ	SLOPE (cal/cc)	x-INTERCEPT (mole fraction)	C _p @ 25°C (cal/mol-°C)	Calculated At (°C)
C ₃ H ₂ F ₆	1.15	2.65 ± 0.07	0.042		ca 1,250
CH ₃ Cl	1.10	1.12 ± 0.03	0.096	9.73	1,751
CH ₃ Br	1.14	5.31	n/o	10.13	ca 5,900
CF ₃ Br	1.17	≥ 9.92	n/o	16.57	ca 11,400
CF ₃ I	1.17	7.5	n/o	16.96	ca 8,525

Non-Catalytic Chemical Extinguishants.

Figure 4 presents the data for CH₃Cl. (The first data point appears to be in error, and not indicative of a catalytic process; this possibility will be reexamined.)

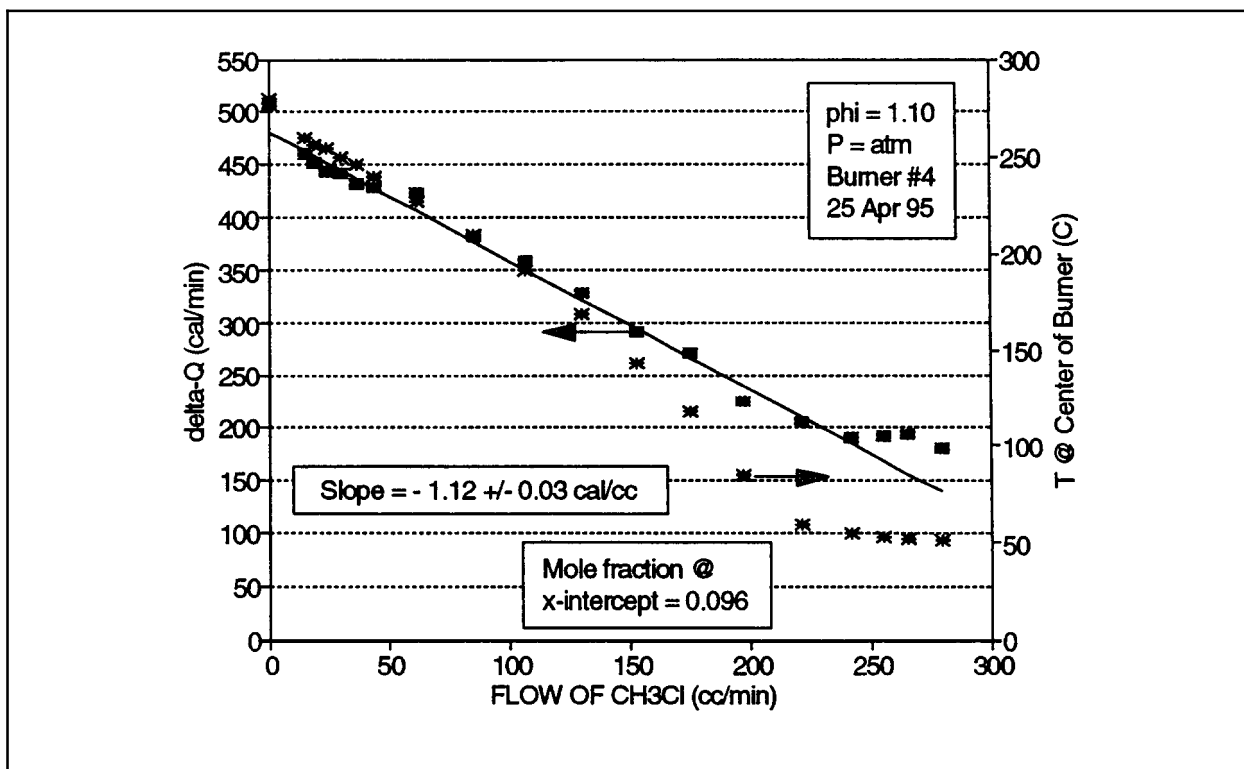


Figure 4. Quenching by CH₃Cl

The data for CH_3Cl are reminiscent of a physical extinguishing agent; however, the calculated temperature of the CH_3Cl (1750°C) is too high, especially when compared with the temperatures calculated for the typical physical extinguishants listed in Table 1. CH_3Cl seems to represent a third type of behavior, in which each CH_3Cl molecule is involved in the same number of chemical quenching "events;" this would explain why the energy decrease is a linear function of the amount of CH_3Cl added.

One additional feature of Figure 4 is worthy of note; at about the **225 cc/min** point, it appears that the characteristics of a fuel-rich flame have again been encountered. Recall the fuel rich experiment with nitrogen, illustrated by Figure 2. It is known that CH_3Cl is flammable. The characteristics of CH_3Cl were further illustrated by an experiment with a fuel rich flame; the results are presented in Figure 5. For

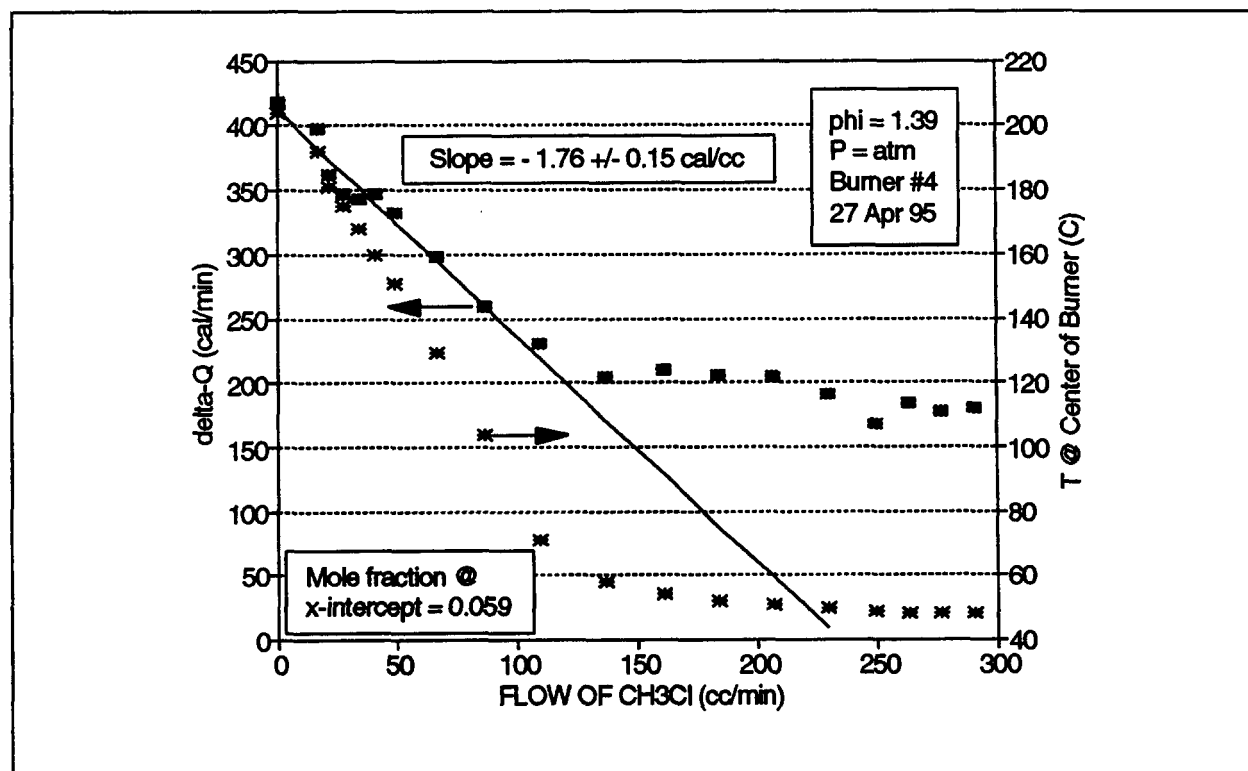


Figure 5. Quenching of a Rich Flame by CH_3Cl

CH_3Cl flow rates greater than **125 cc/min**, the flame lifted off at the center, but remained attached around the periphery of the burner, suggesting as before that the fuel and CH_3Cl were continuing to burn in the presence of entrained oxygen. To confirm this hypothesis, the burner was reconfigured so that the flame would burn in a

slow-flowing nitrogen atmosphere. The results are displayed in Figure 6. The

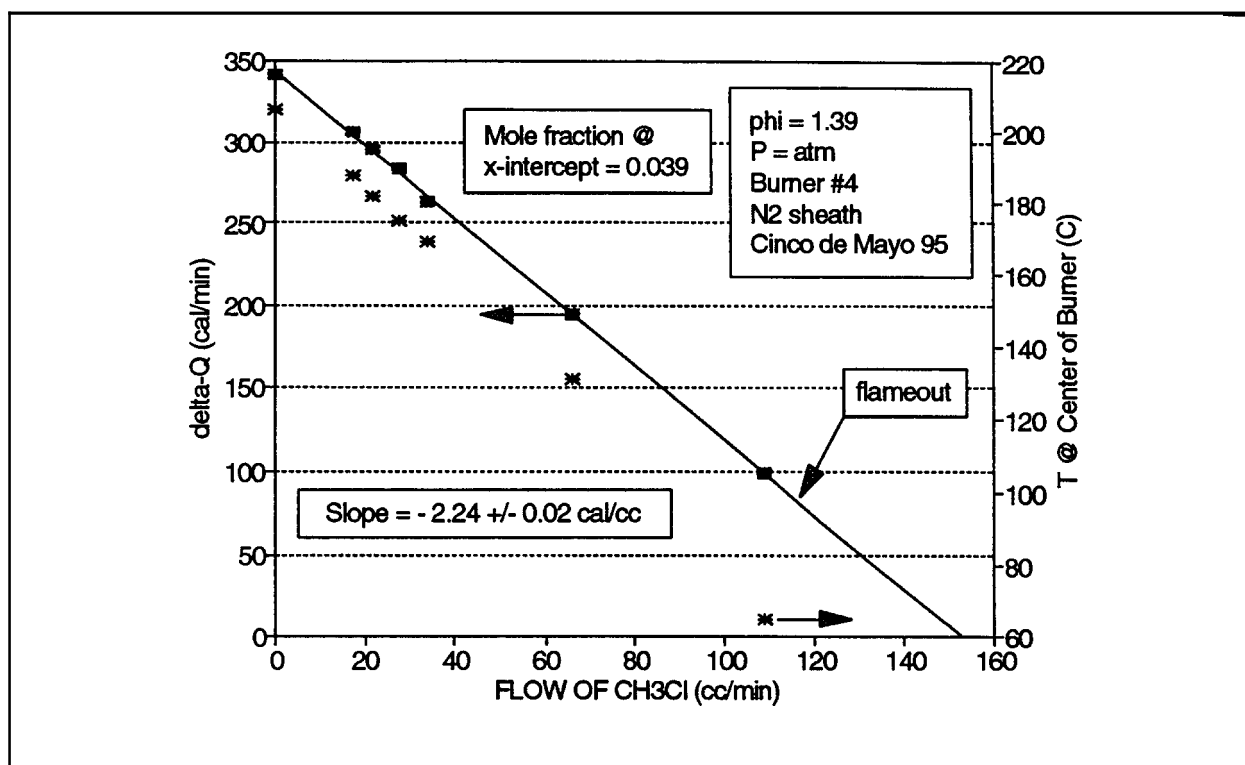


Figure 6. Quenching of a Nitrogen-Sheathed Rich Flame by CH_3Cl

behavior attributed to entrained oxygen was completely absent. It is also useful to note that, when a fuel was added to a flame that was already fuel rich, extinguishment was more easily achieved than in a flame in which the optimum fuel to oxidant ratio had been selected.

One set of results for $\text{CF}_3\text{CH}_2\text{CF}_3$ is shown in Figure 7. At first glance, it appears that this agent is behaving strictly as a physical extinguishant. However, the calculated temperature is significantly (though not unreasonably) higher than the typical values for physical extinguishants. Thus, there may be some chemical contribution in this case; further examination is warranted. There also appears to be an unusual deviation from straight-line behavior early in the experiment. Further information on $\text{CF}_3\text{CH}_2\text{CF}_3$ was obtained in an experiment which was extended to higher flow rates; see Figure 8. The behavior at $\text{CF}_3\text{CH}_2\text{CF}_3$ flow rates greater than 110 cc/min can be reasonably assigned to the fact that this molecule (like CH_3Cl) is both an inhibitor and a fuel. Indeed, at about this point in the experiment, the flame

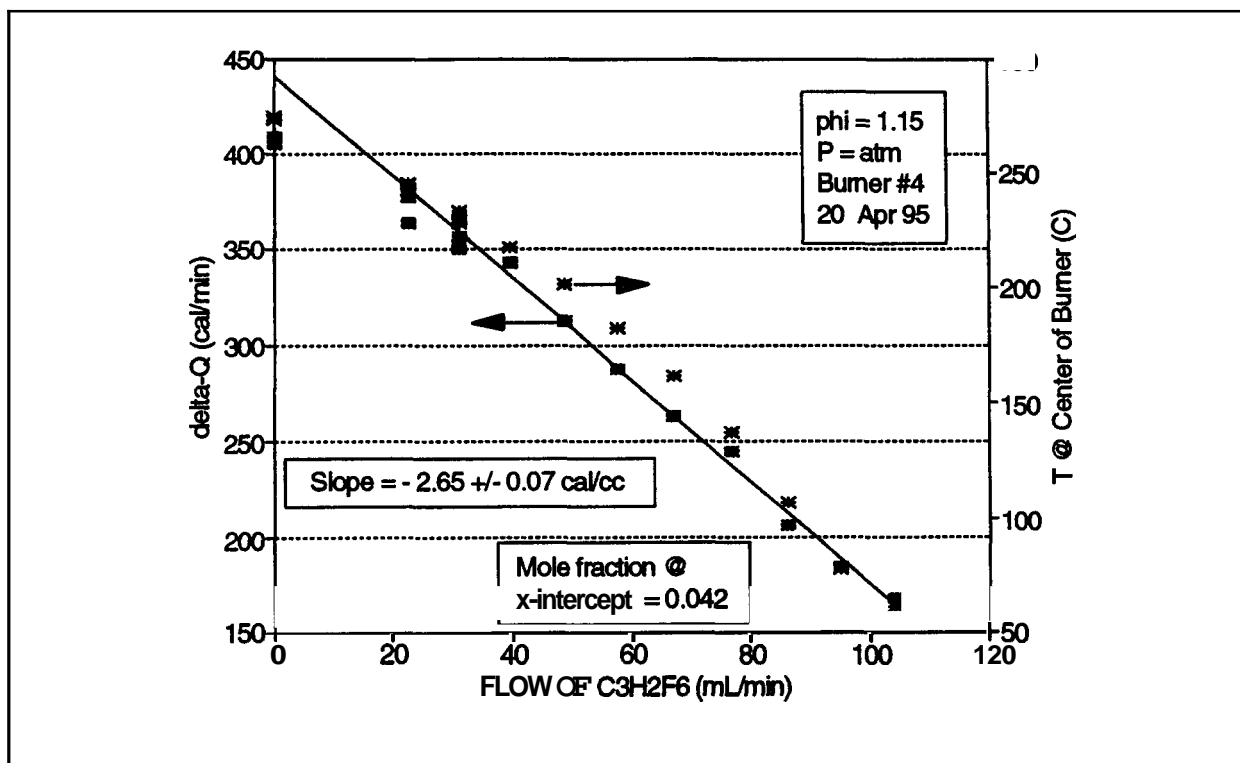


Figure 7. Quenching by $CF_3CH_2CF_3$

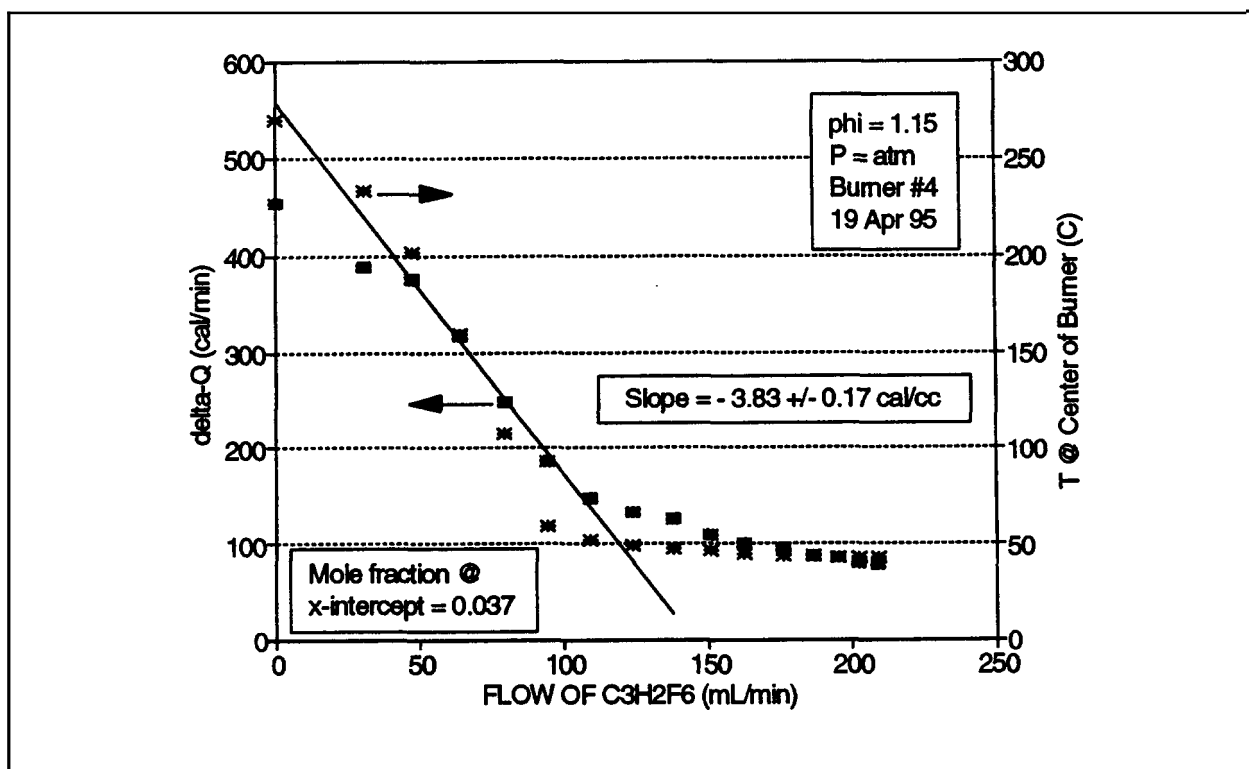


Figure 8. Quenching by $CF_3CH_2CF_3$

developed an incandescent tip in the flame which looked just like a candle flame.

Comparison with Other Results.

Table 3 compares the results of the present work with other published results. The data from the Purdue study represent the amount of agent present in a mixture of the agent with n-heptane and air at its maximum flammability limit. By contrast, the NRL and NMERI data represent the results of cup burner experiments using n-heptane and air. The astonishingly good agreement between the data accumulated in the present work and the data obtained by other workers must be regarded, in part, as fortuitous, since no attempt was made to match the characteristics of the flames in contribution in this case; further examination is warranted. There also appears to be an unusual deviation from straight-line behavior early in the experiment. Further the present work with the flames used in the other experiments reported in Table 3. On the other hand, the fact that the present results closely parallel those accumulated by established techniques serve as a strong indicator as to the effectiveness of the present method.

TABLE 3. COMPARATIVE RESULTS

AGENT	VOLUME % AGENT			
	Purdue ³	NRL ⁴	NMERI ⁵	This Work
He		37		41
Ar		41		73
N ₂		30	31	32
CO ₂	29.5	21	20.4	20
CF ₄	26	16	13.8	14
C ₄ F ₁₀	9.8		5.0	5.4
CF ₃ CH ₂ CF ₃			5.6	≥ 2.8 (note 1)
CH ₃ Cl				5.7
CH ₃ Br	9.7			5.5
CF ₃ I	6.8	3.2	3.0	≥ 1.9 (note 2)
CF ₃ Br	6.1	3.1	2.9	≥ 2.1 (note 2)

Note (1): Estimated from break in curve

Note (2): Estimated from maximum flow rate studied

CONCLUSIONS

The extinguishment of a flame is a remarkably complex process, involving the interplay of hundreds of chemical reactions and numerous physical processes. Ultimately, the experimental results from this study will be tested against theory, using modeling as a key tool. This test against theory will provide additional insight into the implications of the present observations, and will at the same time challenge the theory to correctly describe the observed results. Even in the absence of a detailed theoretical analysis, the present work suggests a valuable tool for measuring the effectiveness of a candidate extinguishing agent, for providing insight into the extinguishment mechanism (or mechanisms) by which the candidate agent suppresses the flame, and for shedding light on the relative importance of the mechanisms, where two are at work at the same time. The present work also permits one to study both fuel rich and fuel lean flames, thus providing additional insight into the extinguishment mechanism(s).

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