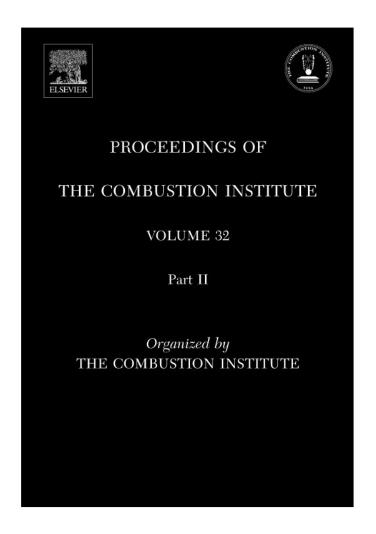
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# Improved understanding of thermal agent fire suppression mechanisms from detailed chemical kinetic modeling with idealized surrogate agents

William M. Pitts\*

National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8662, Gaithersburg, MD 20899, USA

#### **Abstract**

Fire suppression agents that derive their entire effectiveness from physical processes are known as thermal agents. Thermal agents operate by lowering the flame temperature through dilution, heat absorption, and thermal diffusion. Two aspects of these mechanisms are investigated using detailed chemical-kinetic modeling of methane opposed-jet laminar diffusion flames burning in air mixed with two idealized surrogate agents. "X" has the physical properties of argon with the exception of a zero heat capacity. Its only flame effects are through dilution. Results show that X lowers flame temperatures by slowing the combustion chemistry and allowing increased oxygen to pass through the flame sheet. Comparison with results using argon reveals that 59% of argon effectiveness derives from dilution with the remainder due to heat absorption. "Y" is also similar to argon with the exception that it can react to form "Z," which is identical to Y except for having a positive heat of formation. Reaction of Y to Z absorbs heat and lowers flame temperatures. The reaction rate is adjusted using the rate law constants including activation energy in order to control where heat extraction occurs relative to a flame front. Calculated flame temperatures and hence agent suppression effectiveness are found to be insensitive to heat extraction location. The results for X and Y provide strong support for the concept of a well defined limit flame temperature at extinction. It is argued that the conclusions from this modeling study are relevant to coflowing diffusion flames, which are more characteristic of real-world fires.

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Keywords: Diffusion flames; Dilution; Fire suppression; Kinetic modeling; Thermal agents

#### 1. Introduction

The manufacture of halons that have been widely used in fire extinguishing systems was banned in 1994 due to their deleterious effect on stratospheric ozone. As a result, the Department

E-mail address: wpitts@nist.gov (W.M. Pitts).

of Defense through its Strategic Environmental Research and Development Program supported an exhaustive effort, coordinated by the National Institute of Standards and Technology, to improve the understanding of fire suppression and to identify effective replacements [1]. One facet of this program considered thermal agents, defined as those that obtain their effectiveness solely by heat extraction and dilution [2].

<sup>\*</sup> Fax: +1 301 975 4052.

A great deal is known about the effects of thermal agents on flames. The paper by Sheinson et al. provides a good introduction [3]. There are a number of endothermic physical processes that extract heat from a gaseous flame zone, thus lowering the temperature and ultimately leading to flame extinguishment. These include simple heating (i.e., heat capacity) of an agent, phase changes such as vaporization of a liquid or sublimation of a solid, endothermic molecular decomposition (which is classified as a physical process as long as the initial agent and its products do not participate in the combustion chemistry), and simple dilution. The flame temperature is also expected to be a function of the thermal diffusivity of an agent.

This paper summarizes one part of the NIST thermal agents study [2] that used detailed chemical-kinetic modeling of methane planar opposed-jet laminar diffusion flames (POJLDFs) burning in air mixed with idealized, nonphysical surrogate agents to characterize two aspects of thermal agent effectiveness. The first factor, which has been the subject of previous experimental research and analysis, is the relative roles of heat extraction and dilution on the effectiveness of a gaseous thermal agent. Here dilution refers to the ability of a thermal agent to inhibit a flame without extracting heat or directly participating in the flame chemistry.

Sheinson et al. discussed the effects of dilution on extinguishment. [3] They concluded that its effects are relatively small compared to direct heat removal for the thermal agents CF<sub>4</sub> and SF<sub>6</sub>. Zegers et al. suggested that dilution plays a role for relatively inefficient thermal agents such as nitrogen [4]. In the current study the effectiveness of a surrogate thermal agent that dilutes the air but does not extract heat has been investigated. Direct comparison with calculated results for Ar allows the relative roles of heat removal and dilution to be characterized.

Since the important combustion reactions for diffusion flames depend strongly on temperature and take place in regions with high temperature gradients, it is reasonable to hypothesize that the effectiveness of a gaseous thermal agent will vary with the temperature range over which it extracts heat. In order to test this hypothesis, POJLDF flame structures have been calculated for a series of surrogate thermal agents that react unimolecularly to absorb heat. The only difference between the products and reactants is their heat of formation, otherwise both are identical to Ar. Differences between calculated flame structures with Ar and this surrogate agent dilution are directly attributable to the additional heat extracted by the reactive surrogate. By varying the activation energy for the unimolecular reaction, it is possible to modify the location relative to the flame front where heat is extracted and test the above hypothesis. To our knowledge, the effect of heat extraction location has not been considered previously for gaseous agents.

A separate manuscript [5] based on another part of the NIST thermal agents study [2] has been accepted for publication elsewhere. In [5] detailed chemical-kinetic modeling is used to predict the effects of the thermal agents argon, helium, nitrogen and carbon dioxide on methane-fueled POJLDFs. It is demonstrated that the definition of a well defined limit temperature for the maximum flame temperature at flame extinguishment provides quantitative predictions of extinguishing concentrations for POJLDFs and relative agent effectiveness for methane and heptane diffusion flames burning in coflowing air streams.

## 2. Modeling approach

### 2.1. CHEMKIN III and OPPDIF

The widely available code OPPDIF [6] developed by Sandia National Laboratories and now available commercially from Reaction Design<sup>1</sup> was used to calculate POJLDF structure. OPP-DIF solves the pseudo-one-dimensional equations describing an axisymmetric POJLDF. The equations are those originally developed by Kee et al. [7] for premixed flames to solve problems in which the radial velocity gradients in the radial direction are constant at the computational boundaries and were later extended to diffusion flames by Chelliah et al. [8] These equations include initial plug flows for the fuel and oxidizer, which is the assumption treated here. The axial velocity gradients in the axial direction at the burner exits are assumed to be constant.

# 2.2. Detailed chemical-kinetic mechanism for methane

OPPDIF requires a detailed chemical-kinetic mechanism. After reviewing the literature, we chose the widely used methane/air mechanism developed with the support of the Gas Research Institute. The version used was GRI-Mech 1.2. [9] Later versions, GRI-Mech 2.11 with added nitrogen chemistry and GRI-Mech 3.0 with updated reaction data and improved optimization, are available. A comparison of extinction

<sup>&</sup>lt;sup>1</sup> Certain commercial equipment, instruments, or material are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

calculations using the three GRI-Mech mechanisms indicated that the choice of mechanism had minimal effects. GRI-Mech 1.2 consists of 32 chemical species undergoing 177 reactions.

#### 2.3. Surrogate agents

The role of dilution was investigated by mixing air with a surrogate agent, referred to as "X," that has identical properties to Ar with the exception of its heat capacity, which is defined to be zero. Since this species does not extract heat or react, its only effects on the flame are to reduce the collision rates of the other species with each other and to serve as a collision partner for pressure sensitive reactions.

A second surrogate agent, "Y," was used to test the hypothesis that the effectiveness of a thermal agent depends on the location where heat extraction occurs. The molecular weight, thermodynamic properties, and transport properties of Y are identical to those of Ar, but it is capable of undergoing a simple unimolecular reaction to generate a new species, "Z," i.e.,

$$Y \to Z. \\$$

Z is also very similar to Ar, the only difference being that its heat of formation is defined to be positive instead of zero. As a result, the reaction of Y absorbs heat and cools the local surroundings by an amount equal to the heat of reaction,  $\Delta H_{Y \to Z}$ . Since Y and Z do not react with any other species, the reaction is simply a heat sink, and Y therefore meets the definition of a thermal agent.

The rate constant for the reaction of Y is expressed as

$$k_{Y\to Z} = AT^{\beta} e^{-E_a/RT}, \tag{1}$$

where A is the pre-exponential factor,  $\beta$  is the temperature exponent,  $E_a$  is the energy of activation, R is the gas constant, and T is temperature. By varying the parameters A,  $\beta$ , and  $E_a$  it is possible to change the temperature range and rate at which the reaction occurs and hence the location of heat extraction relative to the flame zone. For the calculations which follow, initial values were chosen for A and  $\beta$ , and only the value of  $E_a$  was changed in order to vary  $k_{Y \to Z}$ .

#### 2.4. Extinction calculations

The purpose of these calculations is to characterize the extinction behavior of methane POJLDFs as functions of fuel and oxidizer stream velocities and agent concentration and to use this information to better understand thermal agent mechanisms for inhibiting diffusion flames. Note that we are purposefully distinguishing between the "extinction" of POJLDFs and the "extin-

guishment" of a buoyancy-dominated flame such as a fire.

The burner system modeled consists of opposed flows of fuel (methane) and oxidizer flowing from circular nozzles separated by 2 cm. Since the flow system is axisymmetric, a coordinate system with the axial axis, z, running between the centers of the burner exits and a perpendicular radial axis, r, is appropriate. The fuel exit is located at the origin (z = r = 0) and the oxidizer exit at z = +2 cm with r = 0. For convenience the plug flows at the exits were assumed to have equal velocities of opposite sign. These velocities will be identified by the generic symbol  $U_{\rm b}$  where it is understood that  $U_b$  equals the fuel velocity and the negative of the oxidizer velocity. Temperatures at the burner exits were set to 300 K, and the pressure was 101 kPa.

Extinction of diffusion flames can be understood in terms of the "S" curve originally described by Fendell [10] and Liñán [11]. The name refers to the shape of a plot of maximum flame temperature,  $T_{\rm max}$ , versus Damkohler number, Da, where Da is the ratio of characteristic mixing and reaction times. These authors showed that there are two possible physical solutions for mixtures of fuel and air - combustion and extremely slow reaction regimes. These two branches are connected by an unstable third branch that forms the central part of the "S," but is not physically observable. Starting well up on the burning branch, it is found that  $T_{\text{max}}$  decreases with decreasing Da. As the Da is decreased still further, the temperature begins to drop faster until it ultimately curves onto the middle branch and continues to fall off with increasing Da. Since the middle branch is unstable, the real flame system drops to the lower nonburning branch at the turning point. This transition is interpreted as flame extinction.

The approach adopted here is to computationally identify the flow conditions just sufficient to cause extinction of a flame formed by fuel and either air or air with added agent. Thus the problem becomes one of identifying the turning points for plots of  $T_{\rm max}$  versus Da. Flow velocity, characteristic strain rate, or stoichiometric scalar dissipation rate can also serve as appropriate dependent variables. Since mixing times associated with these parameters are inversely related to their values, the resulting curves are reversed from those for Da plots, with  $T_{\rm max}$  decreasing with increases in these parameters. For these calculations  $U_{\rm b}$  will be employed as the dependent variable.

Since so-called continuation methods [12,13] were not implemented in the version of OPPDIF used, a direct approach was adopted in which higher and higher flow velocities were assumed until either a nonburning solution was found or the differential solver was unable to find a solution. In order to minimize the associated uncertainties, very small incremental increases in

 $U_{\rm b}$  were utilized near the extinction point (the solver is more efficient when an earlier solution for similar conditions is used as the starting point). An arbitrary, but stringent, criterion was adopted which defined the extinction velocity,  $(U_{\rm b})_{\rm ext}$  and temperature,  $(T_{\rm max})_{\rm ext}$  as those for which a burning solution was obtained, but an increase of only 0.01 cm/s in  $U_{\rm b}$  either resulted in a nonconverged or nonburning solution.

Even though thermal radiation provides another mechanism for removing heat from a flame zone, its effects were not included in the current calculations. As discussed extensively in [2] it is expected to have a noticeable effect on flame structure for the conditions relevant to extinguishment of diffusion flames. Detailed chemicalkinetic modeling investigations that incorporate radiation have shown that the relative importance of radiation increases with decreasing strain rate. For the strain rates identified as being typical for extinguishment of buoyancy-dominated diffusion flames, the radiation heat loss represents a relatively small fraction of the total heat release. The neglect of radiation for these calculations does not appear to have seriously limited predictions of extinguishing concentrations, even though its neglect would be expected to change such properties as  $(T_{\text{max}})_{\text{ext}}$  and  $(U_{\text{b}})_{\text{ext}}$ .

#### 3. Results

## 3.1. Surrogate agent with zero heat capacity

Figure 1 shows a plot of calculated  $T_{\rm max}$  versus  $U_{\rm b}$  for various percentages of X added to air. It can be seen that the addition of X reduces the flame temperature. Comparison with comparable results for Ar allows the relative roles of heat extraction and dilution to be characterized. Values of  $(U_{\rm b})_{\rm ext}$  calculated for methane flames burning in air mixed with Ar and X are plotted as functions of the percentage of added agent in Fig. 2. The dilution of air with

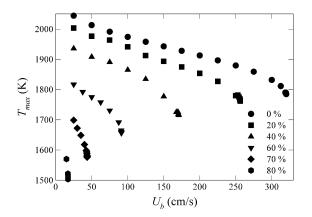


Fig. 1.  $T_{\text{max}}$  plotted against  $U_{\text{b}}$  for methane flames burning in air mixed with indicated percentages of X.

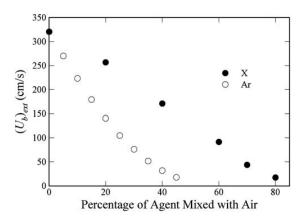


Fig. 2.  $(U_b)_{\text{ext}}$  plotted against added agent percentage for methane flames burning in air mixed with Ar and X.

a fixed percentage of Ar reduces the flame strength more than the corresponding amount of X. Since Ar and X are identical except for their heat capacities, these differences are attributable to the heat extracted from the flame by Ar

Even though there are large differences in the percentages of the two agents that induce extinction for a given  $U_{\rm b}$ , Fig. 3 shows that  $(T_{\rm max})_{\rm ext}$  values are nearly identical. The solid curve in Fig. 3 is from [2,5] and shows a least-squares fit of results for similar calculations using N<sub>2</sub>, Ar, He, and CO<sub>2</sub>. All of the calculated results fall close to this curve indicating each of these thermal agents induces extinction by reducing  $T_{\rm max}$  to a  $(T_{\rm max})_{\rm ext}$  that is nearly constant for a given strained velocity field determined by the corresponding  $U_{\rm b}$ .

It was shown in [2,5] that the assumption of  $(T_{\rm max})_{\rm ext} = 1550~{\rm K}$  provides excellent estimates for the amounts of thermal agent required to extinguish laminar methane opposed flow diffusion flames. Using this value of  $(T_{\rm max})_{\rm ext}$  the extinguishing concentrations for X and Ar are estimated to be 73% and 43%, respectively.

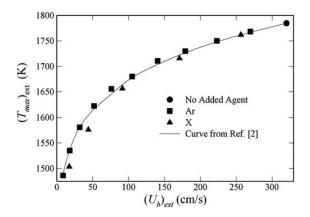


Fig. 3.  $(T_{\text{max}})_{\text{ext}}$  plotted against  $(U_{\text{b}})_{\text{ext}}$  for methane flames burning in air mixed with various percentages of Ar and X. The solid line is a regression fit taken from [2,5].

Assuming that the effects of heat extraction and dilution are additive, as suggested by the data shown in Fig. 3, the effectiveness of Ar is estimated to be 59% due to dilution and 41% due to heat extraction.

The availability of detailed flame structure information from the calculations allows the suppression behavior of X to be better understood. As a starting point, it is important to recognize that flames burning in air and air diluted with X have identical adiabatic flame temperatures. This suggests that reductions in  $T_{\text{max}}$  when X is added must be due to redistribution of the heat generated by combustion over a larger region of space and/or a reduction in the amount of heat released. In order to investigate this point, results for methane flames burning in air and a 40% air/60% X mixture are compared in Fig. 4. It is evident that  $T_{\rm max}$  is reduced by adding X. Since the spatial temperature distributions are similar for the two flames, the reductions in  $T_{\text{max}}$  requires that the ratio of the amount of heat released by the combustion relative to the ability of the combustion gases to absorb heat has decreased.

Figure 5 shows semilog plots of CH<sub>4</sub> and O<sub>2</sub> volume fractions for both flames as a function of z. For both the fuel is completely reacted at the flame surface, while some O2 "leaks" through from the oxidizer side to the fuel side. Liñán and Williams provide an excellent discussion of this behavior and the reasons for it [14]. O<sub>2</sub> reaching the fuel side of the reaction layer eventually diffuses to a location where the temperature is low enough that oxidation can no longer occur. At this point the  $O_2$  is effectively an inert species with the result that less heat is released and  $T_{\text{max}}$  is reduced. Close inspection of Fig. 5 shows that a significantly larger fraction of the available O<sub>2</sub> leaks through to the fuel side of the flame when the oxidizer is X-diluted air. The resulting increased heat extraction explains the reduced  $T_{\rm max}$  calculated for burning in air mixed with X.

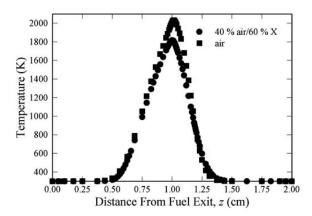


Fig. 4. Temperature plotted against z for methane flames burning in air and a 40% air/60% X mixture.  $U_{\rm b}=25$  cm/s.

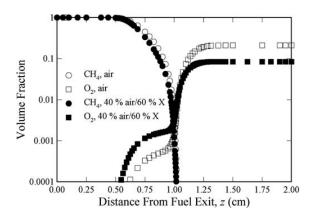


Fig. 5. Log values of methane and oxygen volume fraction plotted against z for methane flames burning in air and a 40% air/60% X mixture.  $U_b = 25$  cm/s.

#### 3.2. Reactive surrogate agent

One difficulty faced in the calculations with the reactive surrogate agent is that the completeness of reaction over a given temperature range varies with the flow conditions due to variations in residence time. For this reason, a set of calculations was performed over a range of  $E_a$  using a single  $U_{\rm b}$ . The relatively low value of 25 cm/s was chosen because this condition results in strain rates similar to those typical of buoyancy-dominated flames. Calculations were run with the A and  $\beta$ parameters in Eq. (1) set to  $1 \times 10^{10}$  cm<sup>3</sup>/(mol·s) and 0, respectively and  $E_a$  values of 25.1 kJ/mol, 58.6 kJ/mol, and 83.7 kJ/mol.  $\Delta H_{Y\rightarrow Z}$  was set to 96.1 kJ/mol. The amount of Y mixed with air was 5%. Figure 6 compares the resulting Y, Z, and temperature profiles across the flame.

It is clear that the majority of heat extraction takes place at low temperatures when  $E_{\rm a}=25.1$  kJ/mol. The conversion of Y to Z is well advanced before the outer edge of the thermal boundary layer is reached at roughly 1.3 cm from the fuel exit, and then rapidly accelerates as the temperature rises. Y has nearly disappeared by the time

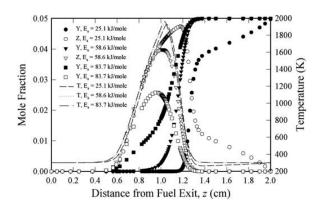


Fig. 6. Y and Z volume fractions and temperature plotted against z for methane flames burning in 95% air/5% Y mixtures having indicated  $E_{\rm a}$ .  $U_{\rm b} = 25$  cm/s.

the temperature increases to 1200 K.  $T_{\text{max}} = 1928$  K, which can be compared to 2006 K when 5% Ar is added to the air.

The reaction behavior of Y is very different when  $E_a$  is increased to 58.6 kJ/mol. Y does not react appreciably until the temperature begins to increase at the outer edge of the thermal boundary layer. As the temperature rises, conversion of Y to Z begins and accelerates with increasing temperature. A substantial fraction of the conversion takes place for temperatures greater than 1600 K, but, even so, the amount of unreacted Y reaching the rich side of the flame is minimal.  $T_{\rm max} = 1934$  K. This is very close to the value with  $E_a = 25.1$  kJ/mol.

When  $E_{\rm a}$  is increased to 83.7 kJ/mol the conversion of Y to Z becomes so slow that a substantial fraction of Y passes through the high temperature zone without conversion to Z. As the temperature falls on the rich side of the flame, the reaction slows down, and the remaining Y becomes kinetically "frozen" and simply diffuses toward the fuel side. As a result, the amount of heat absorption is less than when Y fully reacts. This is reflected in a  $T_{\rm max}$  value of 1963 K, which is intermediate between those found for Y with lower  $E_{\rm a}$ 's and that for a 95% air/5% Ar mixture.

Figure 7 shows  $T_{\text{max}}$  as a function of  $E_{\text{a}}$  for calculations performed with 5% Y added to the air. For  $E_a \leqslant 50 \text{ kJ/mol}$   $T_{\text{max}}$  values are constant within the expected small variations between calculations. As  $E_a$  increases further,  $T_{\rm max}$  begins to increase. As we have seen, this is due to some fraction of Y passing through the flame to the rich side without reacting to form Z. Since the temperature range over which the heat is absorbed by reaction of Y to Z varies widely as  $E_a$  increases from 25 to 50 kJ/mol, these findings show that  $T_{\rm max}$  and, by extension, flame extinction depend only on the amount of heat extracted and not where it occurs relative to the flame zone. Thus the original hypothesis concerning the role of heat absorption location by gaseous thermal agents on extinguishment is disproved.

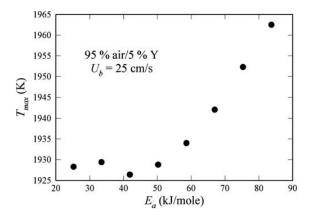


Fig. 7.  $T_{\text{max}}$  plotted against  $E_{\text{a}}$  for methane flames burning in 95% air/5% Y mixtures.  $U_{\text{b}} = 25 \text{ cm/s}$ .

A complete set of calculations similar to those shown in Fig. 1 was carried out for species Y with  $\Delta H_{Y\rightarrow Z} = 96.1 \text{ kJ/mol}$  and  $E_a = 41.8 \text{ kJ/mol}$ . Based on  $(T_{\text{max}})_{\text{ext}} = 1550 \text{ K}$ , the extinguishing volume fraction for Y in air is estimated to be 15.9%. The corresponding value for Ar is 43%. Thus the heat extracted by the reaction of Y to Z reduced the amount of agent required by nearly 2/3. Figure 8 compares calculated  $T_{\rm max}$  as a function of  $U_{\rm b}$  for 15%, 30%, and 45% added Ar with the corresponding results for 5%, 10%, and 15% added Y. The two sets of curves fall close together, but the agreement is not complete. At the lowest concentrations the results for Y fall slightly below those for Ar, while the opposite is true for the highest concentrations. This behavior is most likely associated with expected differences in the contribution of dilution to extinguishment for these two agents.

The effect of doubling the amount of heat absorbed by the reaction of Y was investigated by repeating the calculations with  $\Delta H_{Y\to Z} = 192.1$ kJ/mol. The extinguishing volume fraction for Y was estimated to be 9.7%. This value is roughly 60% of that found with  $\Delta H_{Y\to Z} = 95.2 \text{ kJ/mol}$ , or 20% higher than would be expected if flame extinguishment were due solely to heat extraction. As above, the explanation for the reduced effectiveness is the effect of dilution. The concentration of an agent required for flame extinguishment decreases as the amount of heat it can absorb increases, but the decreased concentration reduces the contribution of dilution, with the result that the effectiveness of extracting additional heat is partially offset.

When values of  $(T_{\text{max}})_{\text{ext}}$  versus  $U_{\text{b}}$  for air diluted with various concentrations of Ar and Y with  $\Delta H_{Y \to Z} = 96.1$  kJ/mol and 192.1 kJ/mol are plotted against the fuel and oxidizer velocities, the results collapse onto the line shown in Fig. 3 even though the amounts of agent required for extinction vary widely with and have a nonproportional dependence on  $\Delta H_{Y \to Z}$ . This provides additional evidence that  $(T_{\text{max}})_{\text{ext}}$  is determined

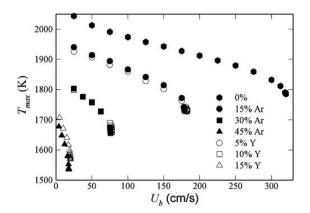


Fig. 8.  $T_{\rm max}$  plotted against  $U_{\rm b}$  for methane flames burning in air mixed with Ar and Y ( $E_{\rm a}=41.8~{\rm kJ/mol}$  and  $\Delta H_{\rm Y\to Z}=96.1~{\rm kJ/mol}$ ).

by local flow conditions and does not vary substantially with thermal agent effectiveness or mechanism.

#### 4. Discussion

The results for the idealized agent X provide a quantitative estimate for the relative importance of dilution and heat extraction (59% versus 41%) for the extinguishment of opposed flow methane diffusion flames by Ar. Since Ar is a relatively heavy monatomic gas, it extracts less heat than polyatomic gases such as N<sub>2</sub>, CO<sub>2</sub> and C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>. For these molecules the larger contributor to effectiveness will be heat capacity, and the role of dilution will diminish with increasing heat capacity.

The reduction in the importance of dilution with an increased ability to extract heat means that there is not a strictly proportional relationship between the effectiveness of gaseous thermal agents and their heat capacity. This nonlinearity should be considered with regard to simple estimates of extinguishing efficiency for thermal agents that are based on heat capacities (either at a constant temperature or integrated over the flame temperature range). If agents are compared that have large heat capacity differences, the agent having the larger heat capacity should be less effective than expected, as observed in the current calculations.

Inherent to these simple approaches for estimating thermal agent effectiveness is the assumption that flame extinguishment and extinction take place when flame temperatures, usually characterized in terms of  $T_{\rm max}$ , are reduced to a well defined limit temperature,  $(T_{\rm max})_{\rm ext}$ . The modeling results indicate this is a robust assumption. Values of  $(T_{\rm max})_{\rm ext}$  have been shown to collapse to a well defined curve when plotted as a function of  $U_{\rm b}$  for Ar, X, and Y even though the ability of these agents to extract heat from the flame zone varied widely. The results agree quite well with a curve taken from a fit for similar calculations using the known thermal agents Ar, He, N<sub>2</sub>, and CO<sub>2</sub> [2,5].

The principal mechanism of flame inhibition due to dilution has been identified as a reduction in the combustion rate that allows more oxygen to break through the flame front to the fuel side and cool the flame zone.

The results discussed here are strictly applicable only for methane POJLDFs where extinction is due to reduction of  $T_{\rm max}$  to a point where homogeneous combustion can no longer be sustained. In a recent study, Takahashi et al. used detailed chemical-kinetic modeling and experiments to show that extinguishment of coflowing methane flames burning in air mixed with Ar, He, N<sub>2</sub>, and CO<sub>2</sub> on a modified cup

burner, an appartus designed to test flame suppression agents on small liquid-fueled flames, occurs when the reaction kernel at the base of a lifted edge flame can no longer anchor the flame in the local velocity field, and the flame blows off [15]. Even though the extinguishment mechanism is not the same as for POJLDFs, agent effectiveness still depended primarily on agent heat capacity. Interestingly, the maximum temperature in the flame kernel remained nearly constant as the concentration of diluent was increased while the maximum flame temperature for the diffusion flame located downstream of the kernel fell. At blow off the downstream maximum flame termperature was considerably higher than the extinguishing temperature identified in the current investigation.

In their internal report, Pitts et al. report similar experimental extinguishing concentration measurements for methane flames burning on Santoro (coflow diffusion flame) and Tsuji (opposed flow) burners [2]. While the extinguishing concentrations for the Santoro burner have similar relative variations with agent as those observed for the modified cup burner [15], lower concentrations of a given agent were required to extinguish the Santoro burner. For a given agent, higher concentrations were required to extinguish the opposed flow flames than were measured for either type of coflow flame. However, the relative effectiveness of the thermal agents was the same for both types of flame. This suggests that the mechanisms responsible for the extinction of POJLDFs and for the blow off of coflowing diffusion flames depend on agent properties in the same way, and POJLDF calculations can be used to predict relative thermal agent effectiveness for both flame types.

The principal finding derived from the calculations involving methane burning in air mixed with Y was that the inhibiting and extinguishing abilities of this thermal agent are unaffected by the location where heat extraction takes place as long as the conversion from Y to Z is complete. The implication of this result is that only the integrated amount of heat absorbed by a gaseous thermal agent as it approaches, enters, and reaches the high temperature zone of the flame needs to be considered.

This conclusion should be contrasted with the results of Lentati and Chelliah whose modeling of methane POJLDFs in the presence of small water droplets indicated that the location where droplet evaporation takes place affect their flame inhibition effectiveness [16,17]. Zegers et al. confirmed this finding experimentally for propane POJLDFs [18]. The contradictory conclusions concerning heat extraction location seem to be associated with the fact that larger water droplets do not follow the oxidizer flow streamlines, whereas gaseous agents do.

As discussed above, conclusions concerning thermal agent mechanisms from modeling of methane POJLDFs are applicable for extinguishment of buoyancy-dominated methane flames. Similar modeling and experimental results to those reported here are presented for propane flames in [2]. Even though the amounts of a given thermal agent required for propane flame extinguishment were shown to be somewhat higher, the relative effectiveness of these agents was very similar for the two flame types. This suggests that the findings from this study should be applicable for a wide variety of fuels.

#### 5. Conclusions

Flame extinguishment by thermal agents has been investigated utilizing idealized gaseous agents designed to test specific aspects of flame extinguishment mechanisms. Results for an agent having zero heat capacity revealed the effects of dilution on extinguishment. The findings show that for the monatomic gas argon the relative contributions of heat extraction and dilution are 41% and 59%, respectively. The importance of heat extraction will increase rapidly as the heat capacity of an agent increases.

Calculations using an idealized reactive thermal agent demonstrated that the location of heat extraction relative to the flame front location did not play a role in flame extinguishing effectiveness.

Plots of maximum flame temperature versus flow velocity for various idealized agents tested collapsed to a single curve. This provides additional evidence that supports the use of a well defined limit  $T_{\rm max}$  for estimating the amount of a thermal agent required to extinguish a flame.

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