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**OAK RIDGE
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**Potential Hazards Relating to Pyrolysis
of c-C₄F₈O, n-C₄F₁₀ and c-C₄F₈ in
Selected Gaseous Diffusion
Plant Operations**

L. D. Trowbridge

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LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
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ABSTRACT

As part of a program intended to replace the present evaporative coolant at the gaseous diffusion plants (GDPs) with a non-ozone-depleting alternate, a series of investigations of the suitability of candidate substitutes is under way. This report summarizes studies directed at estimating the chemical and thermal stability of three candidate coolants, $c\text{-C}_4\text{F}_8$, $n\text{-C}_4\text{F}_{10}$, and $c\text{-C}_4\text{F}_8\text{O}$, in a few specific environments to be found in gaseous diffusion plant operations.

One issue concerning the new coolants is the possibility that they might produce the highly toxic compound perfluoroisobutylene (PFIB) in high-temperature environments. Two specific high-temperature thermal environments are examined, namely the use of a flame test for the presence of coolant vapors and welding in the presence of coolant vapors. A second issue relates to the thermal or chemical decomposition of the coolants in the gaseous diffusion process environment.

The primary purpose of the study was to develop and evaluate available data to provide information that will allow the technical and industrial hygiene staff at the GDPs to perform appropriate safety evaluations and to determine the need for field testing or experimental work. The scope of this study included a literature search and an evaluation of the information developed therefrom. Part of that evaluation consists of chemical kinetics modeling of coolant decomposition in the two operational environments. The general conclusions are that PFIB formation is unlikely in either situation but that it cannot be ruled out completely under extreme conditions. The presence of oxygen, moisture, and combustion products will tend to lead to the formation of CF_4 and oxidation products (COF_2 , CO , CO_2 , and HF) rather than PFIB.

1. INTRODUCTION

The phaseout of the production of chlorofluorocarbons (CFCs) has led to plans to replace CFC-114 at the gaseous diffusion plants (GDPs) with a fully fluorinated coolant. Three candidates are presently being considered: cycloperfluorobutane (also known as FC-c318 or by its chemical formula, $c\text{-C}_4\text{F}_8$), normal perfluorobutane (also known as FC-3110, $n\text{-C}_4\text{F}_{10}$, or simply as C_4F_{10}), and perfluorotetrahydrofuran (also known as f-THF or $c\text{-C}_4\text{F}_8\text{O}$). Two earlier reports documented investigations into the thermal and chemical stability of $c\text{-C}_4\text{F}_8$ at conditions expected to apply during the most severe high-temperature operations at the Portsmouth and Paducah Gaseous Diffusion Plants (Trowbridge 1999a) and in cascade operations (Trowbridge 1999b). This report documents a similar examination of the two additional coolant candidates. Results for $c\text{-C}_4\text{F}_8$ are included for comparison and completeness as well.

Under conditions at which fluorocarbons can thermally degrade (above a few hundred degrees Celsius), potentially hazardous unsaturated fluorocarbon compounds may form, most notably perfluoroisobutylene (PFIB; also known as perfluoroisobutene, octafluoroisobutene, and octafluoroisobutylene, or by its chemical formula, $i\text{-C}_4\text{F}_8$ or $\text{iso-C}_4\text{F}_8$). This degradation has been experimentally observed for $c\text{-C}_4\text{F}_8$, but chemical kinetics studies described by Trowbridge (1999a) suggest that the actual operations examined are unlikely to produce serious concentrations of PFIB. Rather, the main toxic decomposition products are likely to be HF or COF_2 .

GDP coolant losses to the atmosphere occur through both leaks and during maintenance activities and also via leaks into the UF_6 process gas stream and into the cooling water. At process gas conditions, fully fluorinated compounds are even more stable than CFC-114, although a small degree of reaction can be expected. The fluorinating potential of UF_6 guarantees to a good degree of confidence that within the process gas stream, any unsaturated fluorocarbons will be destroyed virtually as soon as they are produced. The coolant reaction products in the process gas stream are thus unlikely to be more hazardous than the parent compound. Possessing no C-Cl bonds, the rate of hydrolysis of any of these coolants leaking into the cooling water stream should be lower than that of CFC-114. At ambient temperatures, all three fluorocarbons are inert to oxidation or hydrolysis in air.

Manufacturer's literature obtained in the late 1980s (DuPont Bulletin B-18B, n.d.); (DuPont Bulletin EL-5, n.d.) suggests that the onset of pyrolysis for $c\text{-C}_4\text{F}_8$ could occur in the temperature range of 250 to 600°C (the lower temperatures applying only when reaction is catalyzed by certain metals). Information on C_4F_{10} and $c\text{-C}_4\text{F}_8\text{O}$ is much less complete but suggests a slightly higher thermal stability. This temperature range is far outside temperatures normally encountered in the diffusion plants except for a few special conditions. These include electrical arcs and open flames (e.g., during welding or accidental fires) and also the operating conditions of the Portsmouth Freon degrader, which is a system that deliberately reacts coolant-containing gas

mixtures with F_2 at high temperature. The Freon degrader, however, has not operated recently and, even when operating, should provide an excess of fluorine, minimizing the formation of hazardous unsaturated fluorocarbons. Another high-temperature environment is that of a propane torch test used to detect coolant vapors in air.

Hazardous levels of PFIB and other less toxic species (unsaturated fluorocarbons, CO , COF_2 , and HF) are available in industrial safety literature. For safety analysis purposes, the issue that must be addressed is the degree to which the coolant reacts to form PFIB or other toxic compounds when exposed to the range of conditions that might occur in or near localized high-temperatures and flames. Definitive information on these points was not located (nor intensively sought) during the CFC replacement campaign of the late 1980s and early 1990s. The earlier thermal stability study on $c\text{-}C_4F_8$ examined the special high-temperature environments using chemical kinetics modeling. That study concluded that the presence of available oxygen would suppress formation of PFIB in favor of COF_2 , CO , and CO_2 (Trowbridge 1999a). This report documents the results of similar studies on the two alternate coolants, C_4F_{10} and $c\text{-}C_4F_8O$. The set of reactions used in this study had to be expanded from that used earlier in order to accommodate the higher degree of fluorine saturation in C_4F_{10} and the presence of oxygen in $c\text{-}C_4F_8O$. Consequently, to provide a closer basis for comparison of the three coolants, the same set of kinetics scenarios were run for all three coolants using the present reaction rate set.

The purpose of this report is to find and interpret available information to provide a technical basis to the industrial hygiene and safety analysis organizations charged with evaluating the suitability and protective measures to be taken when this new coolant is introduced at the GDPs. This report itself is not intended to constitute that safety evaluation. More specifically, this study reviews scientific literature relevant to the question of thermal decomposition of C_4F_{10} and $c\text{-}C_4F_8O$ in order to improve the technical basis for the safety evaluation of the specific operations previously mentioned short of actual experimental simulation of the operations. As part of this study, a thorough literature search was conducted to uncover the available information and to indicate those areas where further information may be desirable.

2. LITERATURE SEARCH

This section summarizes the more pertinent material found in the literature search. Material included here is that which is relevant to the two coolants C_4F_{10} and $c\text{-}C_4F_8O$. Similar information on $c\text{-}C_4F_8$ may be found in an earlier report (Trowbridge 1999a), which also includes material of a general nature on thermal decomposition of perfluorocarbons, the formation of toxic and nontoxic by-products, and the behavior of those by-products. The detail provided in the earlier report will not be repeated here except as it applies to the behavior of C_4F_{10} or $c\text{-}C_4F_8O$.

It is useful, however, to briefly summarize the findings of that earlier literature search. At elevated temperatures, $c\text{-C}_4\text{F}_8$, and in fact nearly any perfluorocarbon, will thermally decompose to a limited number of fragment species whose chemical reactions determine the reaction products. Conditions under which PFIB has been observed to form typically involve extensive contact times (many seconds to hours) of the perfluorocarbon fumes to temperatures that are elevated but cooler than flame temperatures (e.g., 650 to 750°C). The absence of (or at least plausible complete consumption of) water vapor and oxygen seems to be necessary as well. The presence of water vapor leads to the formation of HF and the presence of oxygen to COF_2 , which are the credible toxic products under most circumstances of interest to the GDPs.

Finally, as an unsaturated fluorocarbon, PFIB is very unlikely to form in an environment containing F_2 . No literature specifically on the reaction of PFIB with F_2 or UF_6 was found, but Rogers (1965) reported reaction rates over the temperature range 220 to 250K of F_2 with two isomers of that compound, *cis*- and *trans*-perfluoro-2-butene ($2\text{-C}_4\text{F}_8$, which is structurally $\text{CF}_3\text{-CF=CF-CF}_3$, in contrast to PFIB, which structurally is $(\text{CF}_3)_2\text{C=CF}_2$). Both *f*-2-butene isomers reacted rapidly with F_2 , forming C_4F_{10} . The activation energy for this reaction is much less than the dissociation energy of F_2 . The rates of reaction for the two isomers were indistinguishable. There is no reason to suspect that the rate of reaction with PFIB would be greatly different from that of these isomers. Extrapolated to room temperature, the lifetime of these compounds would be on the order of milliseconds. The implication is that in the presence of F_2 , unsaturated fluorocarbons very quickly react. UF_6 is a weaker fluorinating agent than F_2 , but the strong expectation is that in high concentrations of UF_6 , unsaturated fluorocarbons would not long survive, particularly at the somewhat elevated temperatures of cascade operations. Given that the thermal environment of normal cascade operations is too cold to produce PFIB, and the chemical environment would rapidly destroy any that somehow were produced, no kinetic studies on that environment were performed as part of this work.

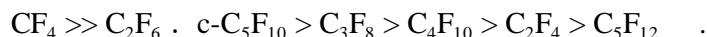
2.1 REACTION RATES

Information needed to evaluate the stability of alternate coolants in the GDP environments includes reaction rates with F_2 , ClF_3 , UF_6 , O_2 , and perhaps related species, in addition to the rate of thermal degradation. The earlier studies on thermal and chemical decomposition of $c\text{-C}_4\text{F}_8$ contain some of the needed reaction rate information, but not all. The rate of reaction of the initial decomposition or reaction of the parent compound, of course, is needed to carry out a kinetic study. A few additional reaction steps need to be included as well due to the increased fluorine-to-carbon ratio in C_4F_{10} and the oxygen content of $c\text{-C}_4\text{F}_8\text{O}$. Part of the literature search was aimed at locating rates for the parent-species reactions, needed product species reactions, or for information which could assist in estimating such rates.

2.1.1 C₄F₁₀ and Related Compounds

The single source found on the reaction kinetics of C₄F₁₀ with F₂ and with UF₆ derives from the GDP coolant replacement program of the early 1990s. A very low rate of reaction of C₄F₁₀ with F₂ was observed at 150°C. No reaction was observed under similar conditions when F₂ was replaced with UF₆ (Trowbridge 1991).

A study of the relative stability of several perfluorocarbons was reported by Steunenberg (1952). In that work, various perfluorocarbons (PFCs) were exposed to a 1000°C filament for several hours, and the rate of decomposition observed. The order of stability determined was



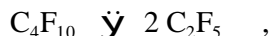
Since it is not clear what fraction of the reactant was exposed to the high-temperature, quantitative rate information cannot conveniently be deduced from this study. No other direct references to rates of thermal degradation or oxidation of C₄F₁₀ were found. A pyrolysis study of the related compound C₅F₁₂ (Rogers 1973) reported the onset of observable decomposition as occurring “above 510°C.” Products identified were C₂F₆, C₂F₄, C₃F₈, C₃F₆, and C₄F₁₀. At 980°C, approximately one third of the initial C₅F₁₂ decomposed during the 200-ms contact time of that experiment.

A rate is given in (Kerr 1981) for the reaction:



which was derived from data taken over the temperature range 297 to 457 K. From this reaction and the thermodynamic equilibrium between the species involved, a forward rate can be calculated. Considerable extrapolation is required from this temperature range to reach the temperatures of interest (800 to 2000 K), so the resulting decomposition rate is of questionable accuracy. Nevertheless, these rates are all that is available and are used in the modeling studies discussed below. As will be shown later, the rate thus derived is consistent with the qualitative observations of stability of this compound.

The reverse of the above reaction,



serves to initiate decomposition, but to estimate the formation of other products in a pyrolysis or high-temperature oxidizing environment, data is needed for additional reaction steps. Rates for a number of such reactions were discussed in the predecessor report (Trowbridge 1999a), and

additional rates were be obtained from data compilations by Kerr (1981) and Burgess (1996).

2.1.2 c-C₄F₈O and Related Compounds

No specific thermal degradation information was found for c-C₄F₈O, and the only experimental reactivity study found yielded a negative result. In the presence of either F₂ or UF₆ at 150°C, no detectable reaction was observed for c-C₄F₈O. Under the same conditions, the related compound CF₃-O-C₃F₇ showed very slight reactivity at the limit of detection, yielding COF₂ and C₃F₈. Expressed as a first-order decomposition, the rate constant at those conditions was calculated to be $6 \times 10^{-7} \text{ s}^{-1}$ (Trowbridge 1993). The implication for the present work is that the structurally similar compound c-C₄F₈O likely will show reactivity at just slightly more severe conditions.

Finding no direct information on c-C₄F₈O, reactivity data was sought for the related perfluoroethers (PFEs): perfluorodimethylether (f-DME), perfluoromethylethylether (f-MEE), and perfluorodiethylether (f-DEE). Experimental information on these compounds is sparse as well. There is considerable interest in the reactivity of PFEs in a tribological environment (that is, reaction with materials of construction – metals or ceramics used in solid state electronics – in the presence of friction). Higher-molecular-weight PFEs are sometimes used for lubricants, especially in solid state electronics and in space applications. Reaction products observed when friction occurs include COF₂, CF₄, and other light PFCs.

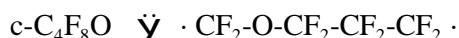
Pure thermal degradation studies have also been conducted on PFEs. For example, a relative rate study on which several C₇ to C₁₂ PFEs and PFCs indicated that the decomposition rate of PFEs was lower than that of corresponding PFCs. In this experimental study, the subject compound was passed through a hot quartz tube at temperatures between 600 and 1000°C. Reported results consisted of the fraction of the reactant decomposed and the identity of reaction products (which predominantly consisted of C₂F₄, C₃F₆, C₄F₁₀, CF₃CFO, C₄F₈ (isomer not specified, but most likely c-C₄F₈), C₃F₈, and possibly C₄F₈O (again, isomer not specified). Unfortunately, flow rate and dwell time information which might have enabled one to deduce quantitative rates were not recorded (Eapen 1997).

Anecdotal information from many sources and relative reaction rate information from a few (Eapen 1997; Trowbridge 93) suggest that PFEs are as chemically and thermally stable in most circumstances as the corresponding PFCs. This implies that the rate of attack of, say, atomic F on the C-O-C moiety is comparable with or lower than the rate of attack on C-C bonds and that C-O bond breakage is no faster than C-C bond breakage.

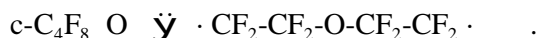
There is some indication that the PFE C-O bond is slightly stronger than C-C bonds. One article (Eapen 1997) cites a reported bond dissociation energy for C-O in f-dimethyl ether of 105.7

kcal/mole (442.3 kJ/mol) but does not give a reference to the source of the information. This value is reasonable for this bond and is too high to be based on a hydrocarbon estimate (for example, the C-O bond energy for CH₃O! CH₃ is 338 kJ/mol) (Weast 1984). Some values for C! C bonds in fluorocarbons are CF₃-CF₃ : 403 kJ/mol; C₂F₅-C₂F₅ : 348 kJ/mol (Chase 1985; Fletcher 1964; Rhodes 1984). Both C- O and C- C bonds are considerably weaker than C-F bonds (e.g., F-CF₃ : 542 kJ/mol; F-C₂F₅ : 527 kJ/mol) (Chase 1985).

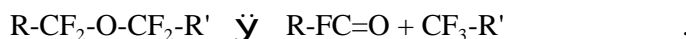
An implication of the comparable stabilities of PFCs and PFEs is that the initiation of decomposition is likely the same, namely attack at or breaking of a C-C bond. The c-C₄F₈O analog to the initial step for C₄F₁₀ decomposition would be



or



The biradical could polymerize, suffer a second bond breakage to form smaller fragments, or abstract F from another molecule to form other products. For PFEs, an additional decomposition route may occur via transfer of F from one C to another near the O:



The mechanism might not occur precisely as stated here, but the end result would be the formation of one fragment containing a carbonyl group and another terminated by -CF₃ (R and R' are either PFC chains or F). The above reaction applied to the first postulated biradical product of c-C₄F₈O, that is $\cdot\text{CF}_2\text{-O-CF}_2\text{-CF}_2\text{-CF}_2\cdot$, would form COF₂ and (after the F rearrangement) CF₃-CF=CF₂, both of which are stable (i.e., not radicals). Analogous mechanisms have been observed in the thermal decomposition of other related PFEs, in particular poly-PFEs. The process is promoted by the presence of strong Lewis acids (e.g., AlCl₃), and apparently to a lesser degree by presence of weaker Lewis acids, including some fluoride or oxide surface layers on metals. There is some controversy about the detailed mechanism. Most published reports implicate Lewis acids as catalyzing this process. Molecular orbital calculations suggest that the energy barrier to decomposition in the presence of a Lewis acid may be on the order of 200 to 330 kJ/mole versus the 400 or more kJ/mole required for direct rupture of the ether C-O bond (Pacansky 1997a; Pacansky 1997b; Waltman 1998).

A few experiments (Ng 1995) and theoretical calculations (Morales 1996), however, suggest that the Lewis acid site itself may not be the culprit, but rather that associated OH groups cause the enhanced reactivity. Whatever the detailed mechanism, there is considerable interest in the catalyzed decomposition of PFEs in presence of metal surfaces with or without oxide or fluoride protective layers. Thermal decomposition appears to occur at lower temperatures in presence of

metal, oxide, Al_2O_3 , or strong Lewis acid (AlF_3 , AlCl_3 , or BF_3) compared with decomposition in their absence.

It is not at all clear how this phenomenon may apply to $\text{c-C}_4\text{F}_8\text{O}$ use in a GDP. In the primary environment, the coolant will be exposed to aluminum and copper, but at temperatures that should be tolerable from a decomposition standpoint. Materials compatibility tests should already have readily revealed such decomposition if it actually were to occur at an appreciable rate at cooler operating conditions. Cyclo- $\text{C}_4\text{F}_8\text{O}$ which has leaked into the cascade should not be greatly subject to attack by UF_6 , simple thermal decomposition, or the catalytic effect of fluorinated metal surfaces, based on the lack of evidence of reaction in the two 1993 experiments (Trowbridge 1993). If decomposition were to occur via either C-C bond breakage or F rearrangement at some low rate (consistent with the 1993 negative result), the products would be similar to or lighter in molecular weight than the parent molecule. The formation rate would be minimal, implying UF_5 formation and deposition would be undetectably low.

2.1.3 Related Pyrolysis and Oxidation Reactions

Linteris (1995) reported an extensive modeling and experimental study of the fate of HFCs (hydrofluorocarbons) and a few PFCs in hydrocarbon flames, the intent being to examine the behavior of these compounds as fire extinguishing agents. The emphasis in the study was on the off-gas composition, and the study involved both kinetic and thermodynamic modeling. The general approach, if not ultimate motivation, of that study was very similar to this present coolant stability study. The level of effort, however, was about an order of magnitude larger than the present effort: about ten times the number of reactions were involved, allowing modeling of the hydrocarbon flame plus the reactions involving fluorine-containing species. There was no explicit list of rates, nor even of the reactions used, but reference was made to an extensive set of rates developed by an NIST group for such modeling purposes (Burgess 1996). This data set, available from NIST (Burgess 1999), contains numerous reaction rates for species containing H, F, C, and O, but no compounds with more than two carbon atoms are considered. The PFCs and HFCs examined in detail in the study were CF_4 , CF_3H , CF_2H_2 , C_2F_6 , $\text{C}_2\text{F}_5\text{H}$, $\text{C}_2\text{F}_4\text{H}_2$, all used as additives in CH_4/air flames. Flame compositions were near stoichiometric, with the HFC inhibitor ranging from 0 to 8 mol %. Except for the case in which CF_4 was the flame inhibitor, all other HFCs and PFCs decomposed stoichiometrically to HF or COF_2 (depending on H availability). Very useful for our purposes is the observation that the F in the HFC or PFC would produce HF when H_2O – either as humidity or as combustion product – was present in excess relative to available F. When H_2O was not in excess, residual F would produce COF_2 .

Linteris (1995) also performed modeling and experimental diffusion flame studies which included both C_4F_{10} and C_4F_8 as flame inhibitors. For these two compounds (and for some other PFCs), the F appearing as the reaction products HF and COF_2 did not account for all the F initially

present in the flame inhibitor. The missing F presumably appeared as other PFCs (e.g., CF_4 , etc.), although the reaction product mix was not analyzed for such PFCs. The authors were interested in the worst case HF production, with the readily hydrolyzable COF_2 being treated more or less as being equivalent to HF. Diffusion flame experimental results for C_4F_8 and C_4F_{10} at 2 mole % (which is the upper concentration limit we consider in our present study) resulted in 60% of the F originally in the PFC appearing as HF or COF_2 . Incidentally, C_4F_8 and C_4F_{10} extinguish premixed propane-air flames at 3.2% and 5.1%, respectively.

Aside from filling a gap in the present study (i.e., jointly modeling the flame reactions and the fluorocarbon interactions in the flame), the NIST work also serves as a useful resource for the rates of many reaction steps involving C-, F-, and O-containing molecules and radicals.

3. KINETICS MODELING

For the present study, a simple model of chemical kinetics was used to evaluate the possibility of formation of PFIB under various conditions representative of those of interest to the coolant replacement program. The model was described in detail earlier (Trowbridge 1999a). Slight modifications of the program were made to accommodate the increased number of reactions and species involved in the present work, but the functionality was otherwise unchanged.

Application of the model to a specific problem requires attention to two additional topics: selection of chemical species and reactions pertinent to the problem and definition of the physical and chemical conditions that apply. The two operational issues in question, namely formation of PFIB in a propane burner used as a test for presence of coolant vapor and PFIB formation during welding operations, each require definition of plausible, or at least bounding, conditions for each scenario (initial gas composition; time-temperature-gas mass flow histories).

Kinetics modeling can be very complex (as in atmospheric chemistry or combustion modeling), sometimes requiring supercomputer-grade computational resources. This model, which was developed for a specific class of problem, runs on a personal computer and is thus somewhat limited in terms of the degree of complexity it can practically handle (i.e., the number of reactions and species, and the degree of “stiffness” of problem, a term relating to the variation between the fastest and slowest rates). The model was written to focus on the formation of PFIB from pyrolysis products of three specific fluorocarbons (although it could do the same for any of the species included in the product mix without alteration of anything but input files). As such, the reaction sets used for the various scenarios neglect or idealize species and reactions that are not directly pertinent to the formation of PFIB. Secondly, the reactions and species chosen incorporate other toxic species (CO , COF_2 , and radical precursors such as F and FCO), although detailed predictions for these species may not reflect reality when factors not considered, such as the presence of H-containing species, are taken into account.

In the previous study (Trowbridge 1999a), the reaction mechanism for the formation of PFIB was discussed, as were the general conditions under which PFIB has been observed to form.

Conducive conditions are those characterized as a pyrolysis environment – high-temperature but lacking other reactants such as water vapor or oxygen. Although a flame environment does not appear to be conducive to PFIB formation, to bound the possible formation rate of PFIB and to allow comparisons between different coolants, scenarios were examined in which the coolants were subjected to the thermal environment but not to the chemical species present (i.e., oxygen and water vapor and, for flame scenarios, common combustion radicals such as HO_2 , O , OH , and CO). In other scenarios, oxygen reactions were included in an attempt to more realistically depict the chemical environment.

3.1 METHOD

The basic strategy of the model is to straightforwardly numerically integrate a set of chemical kinetics equations to track the time evolution of chemical species. The kinetics model is designed to follow the composition of a packet of gas that passes through a specified time-temperature history, as in a streamline passing through a flame or heated zone. The chemical composition at the end of this timeline is the scenario result.

It should be noted that the time-temperature history is an externally specified function in this model. There is no internal feedback between the degree of reaction and the temperature. Heat of reaction (which might warm or cool the gases) is not considered. We are examining scenarios in which the inclusion of coolant is a minor perturbation on other events that thermally dominate the system (e.g., burning of propane or arc welding).

3.2 DEFINING A BASIS SET OF REACTIONS

3.2.1 Pyrolysis Reactions

Pyrolysis of $\text{c-C}_4\text{F}_8$ and other fluorocarbons has been studied and reported extensively in the literature. The previous report in this series (Trowbridge 1999a) discussed reactions and rates pertinent to this process for $\text{c-C}_4\text{F}_8$ and its breakdown products. In that report, a set of reactions and rates was selected for study of the pyrolysis and oxidation of $\text{c-C}_4\text{F}_8$. Most of that set of reactions is used in this study, but additional reaction steps are needed to accommodate the pyrolysis and oxidation of C_4F_{10} and $\text{c-C}_4\text{F}_8\text{O}$. Aside from the obvious need of a rate constant for the initial decomposition of the parent species, additional reactions are needed to account for the increased fluorine content of C_4F_{10} and the oxygen content of $\text{c-C}_4\text{F}_8\text{O}$.

In the earlier study, all reactions and species involving fluorocarbons with a F-to-C ratio higher than 2:1 were idealized and subsumed into the species C_2F_6 . In this study, several saturated

fluorocarbons and their reactions are explicitly considered (C_4F_{10} , C_2F_6 , CF_4), as are the related radicals C_2F_5 and CF_3 , since they are intimately involved in the decomposition mechanism for C_4F_{10} . C_3F_7 and C_3F_8 ought in principle to have been included, but appropriate reaction rate data was not available, so these species were neglected.

The original reaction set used for the study of $c\text{-}C_4F_8$ included reactions numbered from 1 through 9 (and any reverse reactions, numbered, for example ! 1) in Table 1. It also included reactions 19, 26, and 27. Three reactions in the former set were dropped as being either unimportant or composites of multiple steps that are now explicitly included in the new reaction set. Twenty-seven new reaction steps are added to accommodate the new reactants and their breakdown products.

Decomposition of C_4F_{10} is presumed to be initiated with the following step



(the reaction numbers match the reaction steps in Table 1). The rate constant formula for this reaction is derived from the rate constant of the reverse reaction



(Kerr 1981) and the thermodynamic equilibrium, using the thermodynamic parameters for these given by Chase (1985) and Rhodes (1984). Further dissociation of C_2F_5 can occur via the reaction



No rate constant was found for this reaction, but several reactions similar to its reverse reaction,



were found (Burgess 1996), all having rate constants of similar magnitude and possessing no explicit temperature dependence. From trends in those reactions, the estimated rate parameter for reaction ! 11 was derived. The rate constant parameters for reaction 11 were derived from reaction ! 11 and the thermodynamic equilibrium, again using parameters given by Chase (1985).

The behavior of CF_2 is fairly well encompassed by the original reaction set, but CF_3 was not a species explicitly considered. One reaction it may undergo is



Table 1. Reaction rate constant parameters

ID	Reaction	E _A (J/mol)	A ^a	n ^b	References
Part 1					
1	c-C ₄ F ₈ 6 2C ₂ F ₄	331,000	1.000E+17	0	Buravtsev 1985
-1	2C ₂ F ₄ 6 c-C ₄ F ₈	131,000	2.512E+12	0	Buravtsev 1985
2	C ₂ F ₄ 6 2CF ₂	285,000	2.800E+15	0	Schug 1978
-2	2CF ₂ 6 C ₂ F ₄	9,145	4.740E+11	0	Schug 1978
3	C ₃ F ₆ 6 C ₂ F ₄ + CF ₂	345,971	1.580E+13	0	Bauer 1998
-3	CF ₂ + C ₂ F ₄ 6 C ₃ F ₆	31,400	6.457E+09	0	Kerr 1981
4	i-C ₄ F ₈ 6 C ₃ F ₆ + CF ₂	384,920	1.200E+16	0	Bauer 1998
-4	CF ₂ + C ₃ F ₆ 6 i-C ₄ F ₈	238,000	3.981E+12	0	Buravtsev 1989
-4a	CF ₂ + C ₃ F ₆ 6 i-C ₄ F ₈	123,014	8.385E+07	1	Bauer 1998
5	i-C ₄ F ₈ 6 C ₂ F ₆ + (CF) _n	346,017	1.375E+14	0	Atkinson 1957
6	2-C ₄ F ₈ 6 2C ₂ F ₄	417,000	2.512E+11	0	Buravtsev 1989
-6	2C ₂ F ₄ 6 2-C ₄ F ₈	166,000	2.512E+12	0	Buravtsev 1989
7	2-C ₄ F ₈ 6 C ₃ F ₆ + CF ₂	380,000	2.512E+13	0	Buravtsev 1989
-7	CF ₂ + C ₃ F ₆ 6 2-C ₄ F ₈	121,000	7.943E+10	0	Buravtsev 1989
8	1.5 C ₂ F ₄ 6 C ₃ F ₆	188,000	3.162E+10	0	Buravtsev 1985
9	C ₃ F ₆ 6 i-C ₄ F ₈ , 2C ₄ F ₈ , (CF) _n	313,800	1.000E+13	0	Benson 1970
10	C ₄ F ₁₀ 6 2 C ₂ F ₅	328,183	2.765E+15	0.5	derived ^c
-10	2 C ₂ F ₅ 6 C ₄ F ₁₀	-2,577	1.161E+11	0.5	Kerr 1981
11	C ₂ F ₅ 6 CF ₃ + CF ₂	227,925	5.000E+15	0	derived ^c
-11	CF ₃ + CF ₂ 6 C ₂ F ₅	0	4.100E+13	0	estimated ^d
12	C ₂ F ₆ 6 2 CF ₃	384,928	1.862E+17	0	Benson 1970
-12	2 CF ₃ 6 C ₂ F ₆	29,497	1.630E+36	-7.26	Burgess 1996
13	c-C ₄ F ₈ O 6 COF ₂ + CF ₂ + C ₂ F ₄	345,000	1.000E+17	0	estimated ^d
14	CF ₃ 6 CF ₂ + F	565,799	7.595E+22	0	derived ^c
-14	CF ₂ + F 6 CF ₃	0	3.500E+13	0	estimated ^d
15	CF ₃ + F 6 CF ₄	0	1.200E+13	0	Burgess 1996
-15	CF ₄ 6 CF ₃ + F	531,085	1.630E+16	0	derived ^c
16	F + C ₂ F ₄ 6 CF ₃ + CF ₂	0	3.000E+13	0	Burgess 1996
17	F + C ₃ F ₆ 6 CF ₃ + C ₂ F ₄	0	1.202E+13	0	Kerr 1981 ^e

Table 1. continued

ID	Reaction	E _A (J/mol)	A ^a	n ^b	References
Part 2					
18	CO + O + M \rightarrow CO ₂ + M	3,000	6.020E+14	0	Burgess 1996
19	CO + O ₂ \rightarrow CO ₂ + O	159,000	3.090E+11	0	Kerr 1981
20	CO + F + M \rightarrow FCO + M	-2,038	3.090E+19	-1.4	Burgess 1996
21	2 FCO \rightarrow COF ₂ + CO	1,331	2.230E+13	0	Burgess 1996
22	FCO + M \rightarrow F + CO + M	205,016	1.000E+15	0	Keating 1977
23	FCO + O \rightarrow CO ₂ + F	0	3.000E+13	0	Burgess 1996
24	FCO + F \rightarrow COF ₂	0	1.000E+12	0	Burgess 1996 ^f
-24	COF ₂ + M \rightarrow FCO + F + M	323,005	1.780E+14	0	Keating 1977
25	CF ₂ + O \rightarrow FCO + F	4,184	7.000E+13	0	Burgess 1996
26	CF ₂ + O ₂ \rightarrow CO + 2F + O	55,564	2.920E+10	0.5	Modica 1965
27	CF ₂ + O ₂ \rightarrow COF ₂ + O	110,876	1.995E+13	0	Keating 1977
28	CF ₃ + O \rightarrow COF ₂ + F	0	1.862E+13	0	Kerr 1981
29	CF ₃ + O ₂ \rightarrow COF ₂ + F + O	89,956	2.260E+09	1.14	Burgess 1996 ^e
30	C ₂ F ₄ + O \rightarrow CF ₂ + COF ₂	0	1.900E+09	1.0	Burgess 1996
31	C ₂ F ₅ + O \rightarrow CF ₃ + FCO + F	0	2.200E+13	0	Burgess 1996
32	C ₂ F ₅ + O \rightarrow CF ₃ + COF ₂	0	1.100E+13	0	Burgess 1996
33	C ₂ F ₅ + O ₂ \rightarrow CF ₃ + COF ₂ + O	96,232	1.300E+13	0	Burgess 1996

^a Rates are in units of (cm³/mol)^(N-1)/s, where N is the number of moles of reactants in the reaction equation.

^b Rate equations are of the form $k = AT^n \exp(-E_A / RT)$.

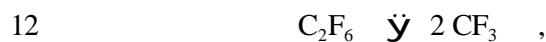
^c derived from ratio of forward and reverse rate constant and equilibrium constant for that reaction.

^d estimated – see text of report for details

^e Reaction products are idealized; see text for explanation.

^f upper limit

The rate for this reaction was given by Burgess (1996), and its reverse,



was given by Benson (1970). The C-F bond energy of CF₃ is similar to that of C-C bonds in fluorocarbons (approximately 368 kJ/mole), and consequently the rate of the reaction



is sufficiently large to require its inclusion in our reaction set. The rate for the reverse of reaction 14,



was estimated from trends in similar reactions (Burgess 1996); the rate for reaction 14 was derived from that rate and the thermodynamic equilibrium. Atomic F may interact with radicals to build saturated compounds. The reaction



completes the formation of CF_4 ; its rate is given by Burgess (1996) and the rate for the reverse reaction was derived from that rate and thermodynamic equilibrium. Atomic F is known to rapidly attack unsaturated fluorocarbons. To represent such reactions,



and



were included, with the rate from the former reaction taken from Burgess (1996) and the latter from Kerr (1981). No rates were found for the further buildup or breakdown of C_3F_7 , so it is assumed that once formed it rapidly converts to CF_3 and C_2F_4 , that combination of products being some 50 kJ/mol more stable than the closest alternative (C_2F_5 and CF_2) requiring no bond rearrangement. A more thorough treatment would have included reactions for the buildup and breakdown of C_3F_7 and C_3F_8 , but that alternative was considered to be a needless complication for the present application. The artificial exclusion of these species is justified on the basis that higher saturated PFCs behave, for our purposes, no differently from those already included.

No direct information was found on the decomposition of $\text{c-C}_4\text{F}_8\text{O}$, but extensive circumstantial evidence suggests that it will be at least as thermally stable as corresponding fluorocarbons. For purposes of analysis, a chemical equation was postulated:

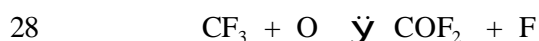
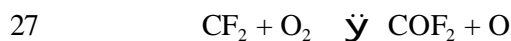
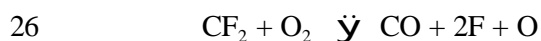
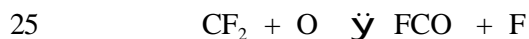
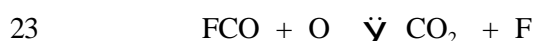
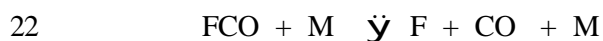
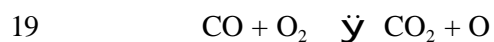


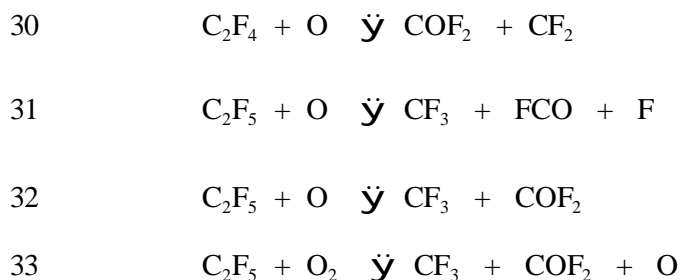
with rate constant parameters estimated to be similar to the other unimolecular rates for higher fluorocarbons. The activation energy is chosen to approximate the C-C bond energy in a relatively unstrained PFC. The specific values chosen for the rate constant parameters make the decomposition of $\text{c-C}_4\text{F}_8\text{O}$ proceed about a third as fast as that of the other two coolant

candidates. Unlike the other two coolants, however, no reverse reaction is included which could lead to its reformation once dissociated.

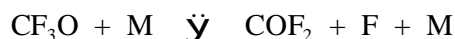
3.2.2 Reactions Involving Oxygen-Containing Species

In the earlier c-C₄F₈ decomposition study (Trowbridge 1999a), a very few oxygen reactions were included. The ones selected were those which were known to be rapid at the conditions of interest and which would react with the key pyrolysis fragments of the coolant. The selection was not intended to be comprehensive but to allow the kinetic model to determine the proportion of reaction products that would form oxidized species rather than remain as pure fluorocarbons. In the present study, there are more fluorocarbon fragment species, many of which participate in known, rapid reactions with oxygen or oxygen-containing species. The following reactions were chosen to represent this class of activity:





Rates for reactions 22 and 24 were taken from Keating (1977); the rates for 19 and 28 were taken from Kerr (1981); 26 is from Modica (1965) and the remainder were taken from the NIST data base (Burgess 1996). The rate for reaction 29 was sufficiently rapid that its inclusion was necessary. The decomposition rate of CF_3O ,



was also given by Burgess (1996). At conditions of interest to this study, this reaction was even more rapid than reaction 29, so rather than introduce a new species (CF_3O) and several more reactions to the model, reaction 29 was idealized as producing COF_2 , F, and O.

Many other reactions were examined but not included in the modeling in this study. Those involving C, F, and O that were not included were discarded because they would not affect the reaction system. That is to say, at the temperatures, pressures, and concentrations of interest, they would not produce or consume species as rapidly as other (included) reactions. For example, O_2 dissociation and recombination were not included because, at the temperatures and time scales of interest, those processes were slow compared with other reactions that produced or consumed O or O_2 .

No reactions or species involving hydrogen are included in this study. To fully model the systems under consideration, species and reactions involving water vapor, HF, HFCs, and hydrocarbons ought in principle to be considered, but such an effort is beyond the resources of this study. The reader is cautioned that in scenarios in which water vapor, hydrocarbons, or combustion products credibly could participate, the model results should not be taken as predicting the actual outcome. From direct and indirect evidence in the literature (Trowbridge 1999a and references therein), it is concluded that PFIB formation cannot be plausibly increased by the presence of hydrogen-containing species, but rather that it would be reduced or eliminated. In that sense, PFIB predictions can be considered as bounding the actual result, within the limits imposed by uncertainties of the kinetic data. On the other hand, HF is the ubiquitous end product of most reactive fluorine-containing species when water vapor or other hydrogen sources are present. For example, fluorine appearing in the product species F, FCO, and COF_2 would probably appear as HF were water vapor considered (and present in sufficient quantity), and the presence of hydrogen-containing species in a high-temperature environment likely would divert some fluorine

away from the formation of stable PFCs and toward the formation of HF.

The model is constructed so that a subset of the reactions listed can be selected in order to compare the results of different postulated mechanisms, rate constant values, or simply to speed up calculations. For example, pyrolysis of a pure fluorocarbon need not include any reaction involving an oxygen-containing species. For all studies discussed in the present report, a single list of reactions and species was used, but for pure pyrolysis cases involving PFCs, species and reactions involving oxygen were not “turned off.”

For each reaction, a formula for the rate constant was chosen from those found in the literature search. The parameters for these formulae are listed in Table 1. Where several rate constant formulae were available, the basis for choosing a particular one was the credibility of that rate for the conditions of interest. In a few cases, there was considerable variability of rates with no clear way to distinguish their relative merits. In such cases, alternate formulations are included, the intent being to choose one rate or the other and compare the outcomes of otherwise identical scenarios. Reactions 8 and 9 fall into this category and were available in the model, but were not used in any of the results reported here, although they were used in sensitivity analyses reported by Trowbridge (1999a). Similarly, two rate constant formulae for reaction ! 4 are included in the model from two sources, giving disparate rate constant parameters for the same reaction step. The base case rate constant used for reaction ! 4 was provided by Bauer and Javanovic (1998), listed as ! 4a in Table 1. It is not necessarily more reliable than the other formula, ! 4, but is more conservative in that it predicts faster production of $i\text{-C}_4\text{F}_8$.

3.3 TIME-TEMPERATURE PROFILES

The two defined high-temperature operations identified in which a coolant vapor might be exposed to high-temperatures are (1) a propane burner used as a flame test for the presence of coolant and (2) Metal-Inert Gas (MIG) welding performed in the presence of ambient coolant vapor. The MIG welding operation was further subdivided into the environment in the vicinity of the weld (i.e., ambient air, including coolant, mixing with the stream of heated inert cover gas) and the “trans-weld” environment (i.e., gas in contact with the metal surface of the part being welded but on the opposite side from the actual welding operation).

Each of these environments can be defined in terms of an idealized time-temperature history in which the coolant-containing gas is rapidly heated, remains at high-temperature for a period, then more slowly cools. Data were available to characterize the propane burner and trans-weld scenarios fairly reliably. The weld-side scenario is less well characterized, but temperature time lines were postulated which can be expected to bound the actual behavior.

3.3.1 Propane Burner Time-Temperature Profile

A propane torch with a special “Halide Leak Detector” burner tip (manufactured by BenzOmatic of Medina, New York) is presently used to test for the presence of coolant in the air. It functions by mixing propane with air (the air possibly containing coolant vapor) and burning it with the flame directed at a heated copper disk. Color changes in the flame are indicative of the presence of halogen-containing gases. The problem at hand is to estimate (or at least to bound) the production of PFIB in the torch’s exhaust gas.

Details of the physical model of this propane flame are described in detail by Trowbridge (1999a). Briefly, a temperature-vs-time profile was devised to approximate the thermal history the gas would experience as it transits the burner flame in a typical streamline. The specific parameters used in the model are listed in Table 2. In the streamline, the gas entering the flame front is assumed to instantly rise from ambient temperature to 1400°C, to remain at that temperature for 0.002 s, and then decline at a rate of 20,000°C/s until it reaches 400°C, where it

Table 2. Parameters for temperature-vs-time profile used for the three scenarios

Scenario	T_{\max} (EC)	time at T_{\max} (s)	T_{decline} (EC/s)	T_{\min} (EC)
Propane burner	1400	0.002	−20,000	400
MIG weld (cover gas)	700	0.01	−2,000	500
	1000	0.01	−5,000	500
	1500	0.01	−10,000	500
MIG weld (Trans-weld)	400	3	−3.33	200
	450	3	−4.17	200
	500	3	−5	200
	700	3	−8.33	200
	1000	3	−13	200
	1250	3	−18	200

remains for the remainder of the 0.1-s total simulation time. This temperature-time profile is an idealized representation of the thermal environment experienced by gas passing through the center of a propane burner flame.

3.3.2 Weld-Side Scenario Time-Temperature Profiles

Two MIG welding scenarios were defined (with many variations used to explore uncertainty or variability in operating parameters). The two scenarios are intended to depict the environment on the “weld side” (i.e., where the welding is taking place) and on the “trans-weld” side (i.e., the side of the plate or pipe opposite the welding). For each scenario, time-vs-temperature profiles were defined based, where possible, on historical measurements and on welding literature.

MIG welding is a variety of arc-welding in which a cover gas (generally a mixture of argon and CO₂) floods the area being welded, preventing air (and, incidentally, coolant vapors) from reaching the molten region of the weld. The process inevitably will heat the cover gas in the vicinity, which will rapidly flow away from the weld, in the process mixing with cooler cover gas and ambient air. Defining the thermal and composition history of a representative collection of gas streamlines is a very complicated endeavor. If there is coolant vapor in the ambient air, qualitatively, we can say that low concentrations and quantities of coolant would be exposed to higher temperatures, and higher concentrations and quantities of coolant would be exposed to lower temperatures. In all cases, where there is coolant, there is oxygen (and, likely, water vapor), there being no mechanism to deplete the oxygen other than by reaction with coolant.

In the previous study (Trowbridge 1999a), three time-temperature profiles were defined for this scenario, and these will be adopted here. The time line was based on cover-gas volume flows and dimensions. The idealized time-temperature profile is as follows: an instantaneous temperature rise is followed by 10 ms at the defined maximum temperature, then by a 100-ms decline to 500°C. This would represent the thermal environment within the first 10 to 20 cm of the gas flow path. The maximum temperature was varied widely from 1500°C (near the melting point of iron and probably unrealistically high) down to 700°C, which may better represent the most severe thermal environment experienced by significant coolant concentrations. From consideration of heat capacities, a 50-50 mixture of MIG weld cover gas heated to 2000 K and ambient-temperature air with 2% coolant would yield a temperature (barring other heat loss mechanisms) of about 800°C. More realistic temperatures would involve mixing air with cover gas that is never heated to this extent. The wide variation in maximum temperature is intended to compensate for the uncertainty in the thermal history. The specific parameters used are listed in Table 2.

3.3.3 Trans-Weld Scenario Time-Temperature Profiles

The chemical environment on the side opposite the weld is easier to define. A variable quantity of coolant vapor will be present in ambient air (or possibly in an inert purge gas). This gas will be in contact with a hot spot near the region of the weld. The temperature of the metal at any given location on the path of the weld will rise fairly quickly to a maximum and then fall more slowly as the welding passes by its location. Such temperature-time histories have been recorded in welding literature and GDP experience and formed the basis for the idealized time-temperature profile used here. This profile assumes an instantaneous rise to a maximum temperature that is maintained for 3 s, followed by a decline to 200°C over the next minute. Typical maximum temperatures observed in an earlier welding test were on the order of 420 to 480°C (Underwood 1996). Allowing for variations in weld speed, material thickness, etc., one might plausibly expect peak temperatures of up to 700°C. For purposes of conservatism, peak temperatures of up to 1250°C were used.

The time-temperature profiles used assume that the gas adjacent to the weld remains in place and is heated to the material temperature. Depending on the orientation of the surface, convection currents plausibly would be expected to mitigate the gas heating somewhat, but that is not considered here.

The trans-weld scenario is the least likely to result in direct exposure of personnel (being typically on the inside of welded equipment). Involving longer times, intermediate temperatures, and in the case of an ambient inert gas rather than air, it is the only environment examined which has a realistic possibility of producing PFIB in significant concentration. (Pyrolysis scenarios in the propane burner case are unrealistic from this point of view due to the known but neglected presence of water vapor.)

3.4 PROPANE FLAME (HALOGEN TESTER)

3.4.1 Scenario Definition

Propane burner scenarios varied in the choice of coolant and in the initial concentration, which was chosen to be either 1,000, 5,000, or 20,000 ppm (all ppm figures are mole-based, not mass based). Two classes of propane burner scenarios were run. One class was pure pyrolysis (i.e., heat only). In that class, the starting concentration of coolant was subjected to the specified thermal environment and the chemical kinetics model allowed to operate. That environment is representative of the thermal, but not the chemical, environment experienced in a propane flame. All accessible reactions were permitted to operate except, as mentioned earlier, reactions -4, 8, and 9, and for $c\text{-C}_4\text{F}_8$ and C_4F_{10} , any reactions involving O-containing species. The pyrolysis cases do not provide a realistic indication of the formation of PFIB in the propane burner, as they neglect oxygen, water vapor, and other hydrocarbon and combustion product species. They are useful, however, in giving a relative indication of the PFIB-forming propensity of one coolant over another and could be applicable in situations not directly examined in the current study.

The second class of reactions added oxygen to the starting mixture. Most such cases included 27,000 ppm (2.7%) O_2 in the initial reactant mixture, a figure chosen as an arbitrary but plausible value for oxygen unconsumed in the combustion of propane. Two such cases used a lower value (5,000 ppm) to explore the effect of complete oxygen consumption by the coolant.

For each case, a specific inlet concentration of coolant (and, if appropriate, oxygen) is postulated, as discussed previously. For species initially absent, a starting composition greater than zero must be specified for computational reasons. This value was set at 0.1 ppb for all runs and does not materially affect any results larger than a few tenths of a part per billion. Tabular results down to 1 ppb are reported, so these initial nominal quantities do not affect the tabular output.

3.4.2 Pyrolysis Cases

The results of all cases are listed in Appendix A, Table A.1. Key results are more succinctly summarized in Table 3. Column 1 indicates the coolant considered in that case. Column 2 indicates the reaction rate set (either “pyrolysis” - that is, not including oxygen reactions - or “oxygen,” including the fluorocarbon and oxygen-involved reactions). The next two columns indicate the initial concentrations of coolant and oxygen (zero in these scenarios). The next three columns list the final concentrations of the three major stable toxic species considered in the model, PFIB (i! C₄F₈), COF₂, and CO. Finally, the two or three largest products (other than the toxic species) are listed.

Pyrolysis results for c-C₄F₈ typically indicate a higher propensity for the formation of PFIB than do the other two coolants. C₄F₁₀ produces nearly as many moles of CF₄ as there are initial moles of C₄F₁₀ (see Table A.1). The remainder of the molecule fragments largely to CF₂ at high-temperature and for all intents and purposes, behaves as if there had originally been 3 moles of c-C₄F₈ for every 4 moles of C₄F₁₀ actually present at the outset. For the c-C₄F₈O reactions, even though there was no O₂ present in the initial gas mix, the presence of O in the formula of the molecule required inclusion of oxygen species and reactions. The results predict that the oxygen in c-C₄F₈O appears quantitatively as CO. Ultimately, the products include nearly a mole of CF₄ per mole of initial c-C₄F₈O. The remainder of the molecule behaves as if there had been 1 mole of c! C₄F₈ initially for every 2 moles of c! C₄F₈O initially present.

The quantity of PFIB produced in the kinetic runs was found in an earlier study on c-C₄F₈ pyrolysis (Trowbridge 1999a) to correlate with what was termed “available CF₂.” This trend continues for the two additional coolants examined here. Available CF₂ we will define as the concentration of CF₂ that would exist if the fluorocarbon were fragmented completely to CF₂ after accounting for C or F consumed in the formation of other stable end products such as CF₄ or, in the case of c-C₄F₈O, CO. Thus for each mole of c-C₄F₈, full fragmentation to CF₂ yields 4 moles of CF₂. For C₄F₁₀, the excess F atoms will remove one C as CF₄, leaving 3 moles of CF₂ available per mole of C₄F₁₀. For c! C₄F₈O, one carbon is removed to form CO, and another to form CF₄, leaving 2 moles of CF₂ per initial mole of c! C₄F₈O. Figure 1 depicts this trend using the results of the three initial concentration cases listed in the pyrolysis section of Table 3. Data points (PFIB produced versus available CF₂) are shown along with a regression fit:

$$[\text{PFIB}] = 4.2 \times 10^{-13} [\text{CF}_2]^{2.92}$$

where [PFIB] is the predicted final concentration of PFIB and [CF₂] is the available CF₂, as discussed above (both concentrations being in units of mole ppm). The differing propensity of these coolants to form PFIB can thus be roughly predicted, and the variation between the results

Table 3. Summary of results for propane burner -- Pyrolysis cases

(all quantities are in mole ppm unless otherwise indicated)

Coolant	Rate set	Initial		Final			Other major product gases	Notes ^a
		Coolant	Oxygen	PFIB	COF ₂ ^a	CO ^a		
c-C ₄ F ₈	Pyrolysis	1,000	0	0.014	—	—	C ₂ F ₄	
C ₄ F ₁₀	Pyrolysis	1,000	0	0.005	—	—	CF ₄ , C ₂ F ₄	
c-C ₄ F ₈ O	Oxygen	1,000	0	0.001	—	1,000	CF ₄ , C ₂ F ₄	
c-C ₄ F ₈	Pyrolysis	5,000	0	2.09	—	—	C ₂ F ₄ , C ₃ F ₆	
C ₄ F ₁₀	Pyrolysis	5,000	0	0.90	—	—	CF ₄ , C ₂ F ₄ , C ₃ F ₆	
c-C ₄ F ₈ O	Oxygen	5,000	0	0.26	—	5,000	CF ₄ , C ₂ F ₄	
c-C ₄ F ₈	Pyrolysis	20,000	0	57.6	—	—	C ₂ F ₄ , C ₃ F ₆	
C ₄ F ₁₀	Pyrolysis	20,000	0	31.7	—	—	CF ₄ , C ₂ F ₄ , C ₃ F ₆	
c-C ₄ F ₈ O	Oxygen	20,000	0	12.6	—	20,000	CF ₄ , C ₂ F ₄	

^aPyrolysis cases are included to provide a basis for comparison of coolants but are not considered to realistically reflect the outcome of coolant passage through a propane burner flame, as combustion products of the propane fuel are not included.

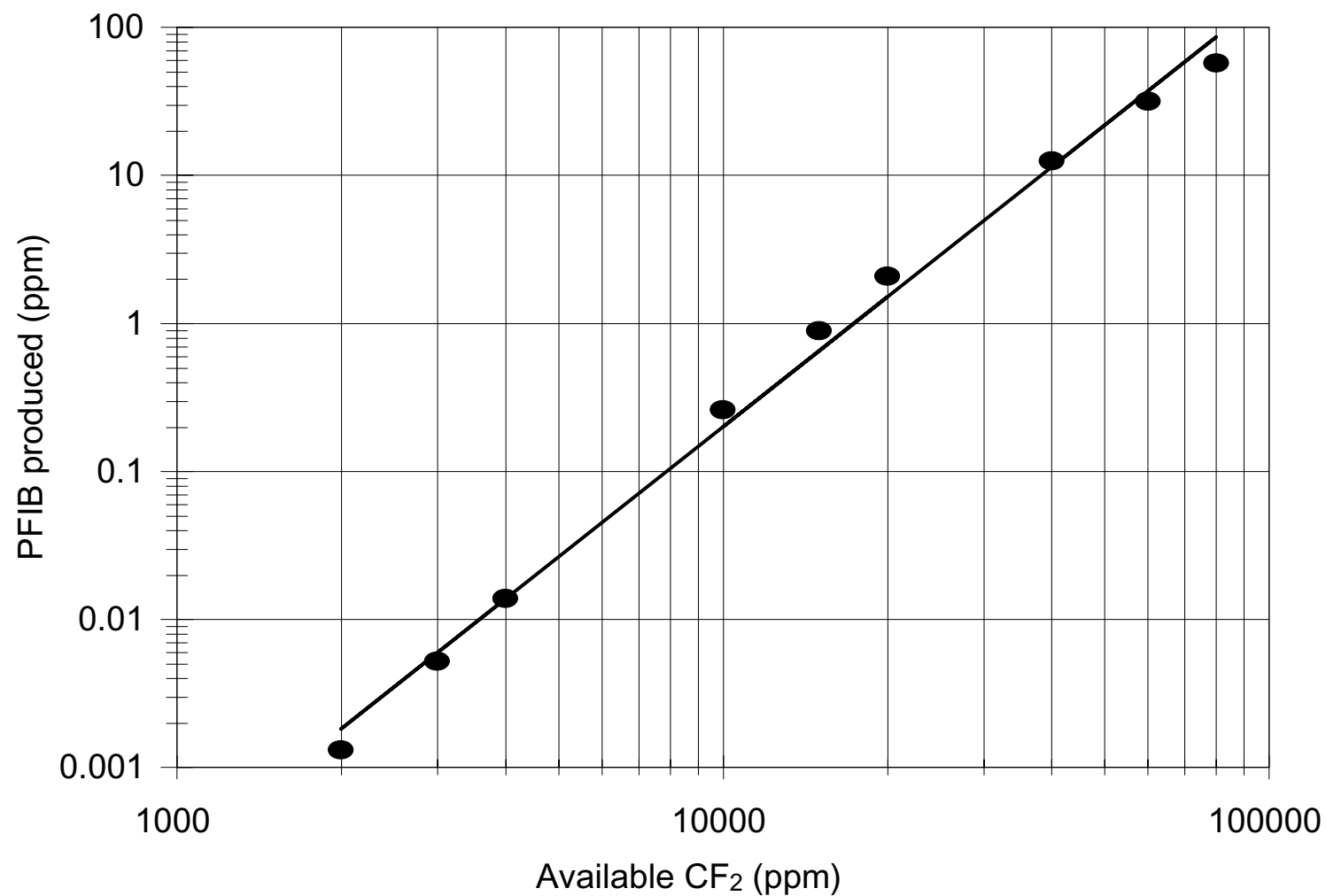


Fig.1. Correlation between PFIB formation and available CF₂ (as defined in the report) for low-or no-oxygen pyrolysis scenarios.

is conveniently explained. This trend, of course, assumes that the fluorocarbon gets hot enough, for a long enough period to fully fragment and react to its pyrolytic endpoint. The trend also assumes anaerobic pyrolytic conditions, which is to say, little or no oxygen.

A more detailed look at the evolution of reaction products under pyrolytic conditions is depicted graphically in Figs. 2 (radicals and oxidizers) and 3 (stable fluorocarbon species) for a brief period at the beginning of the run for a typical case (5000 ppm C_4F_{10}). These figures illustrate some important features of a flame temperature environment regarding fluorocarbon pyrolysis. In a very short time, most of the coolant decomposes to C_2F_5 , which in turn decomposes to F, CF_2 , and CF_3 . Secondary and tertiary products (CF_4 and C_2F_4) reach steady-state values at fairly low concentrations in less than 1 μ s. The compound C_2F_6 is formed early at high concentration, but begins a decline in favor of formation of additional CF_4 and CF_2 . PFIB declines slightly from its nominal initial concentration of 1 ppb. It can be seen from these figures that flame temperatures do not favor formation of PFIB. Only when the gas cools sufficiently for formation of larger concentrations of C_3F_6 does the PFIB increase in concentration.

Figures 4 (radicals and oxidizers) and 5 (stable species) show the evolution of products for the same case up to the end of the simulation at 0.1 s. CF_4 reaches and remains at its high-temperature value very early, having consumed most available excess F and CF_3 . Higher carbon-containing species begin to reform only as the gas cools. As the temperature declines, various reaction rates decline to the point that different products cease being formed. Between 1200 and 700°C, most product compositions stop changing until, at the final temperature (400°C), only the slow combination of remaining trace levels of CF_2 and C_2F_5 persists. In particular, PFIB ceases to form below about 900°C under these conditions. This suggests that in a pyrolysis environment, the maximum temperature is not critical if it exceeds a certain level (about 1400°C). It is the time spent within a critical temperature range that favors the formation of PFIB.

The observation that peak temperatures higher than 1400°C did not change the outcome but greatly lengthened run times led to the decision to run the models at that temperature, rather than at higher temperatures more accurately reflecting peak propane flame temperatures.

Although c- C_4F_8 was examined earlier and in somewhat more detail, cases involving c- C_4F_8 were rerun in the present study so that a uniform basis for comparison of the three coolants would be available. The scenario definitions in this report are similar but not in all cases identical to the earlier study, and a few reaction rates have been altered, either as to the selection of rate constant parameters or the degree of idealization of reaction products. A few selected cases were run under both the old version of the reaction/species set and the new version, selecting as closely as possible the same reactions. The outcome in terms of final concentration for any species typically differed by a few percent of its value and at worst (for some minor inert products involved in reactions whose rates had been changed) by a few tens of percent. Using the new, expanded reaction set (with many additional species and reactions) changes the

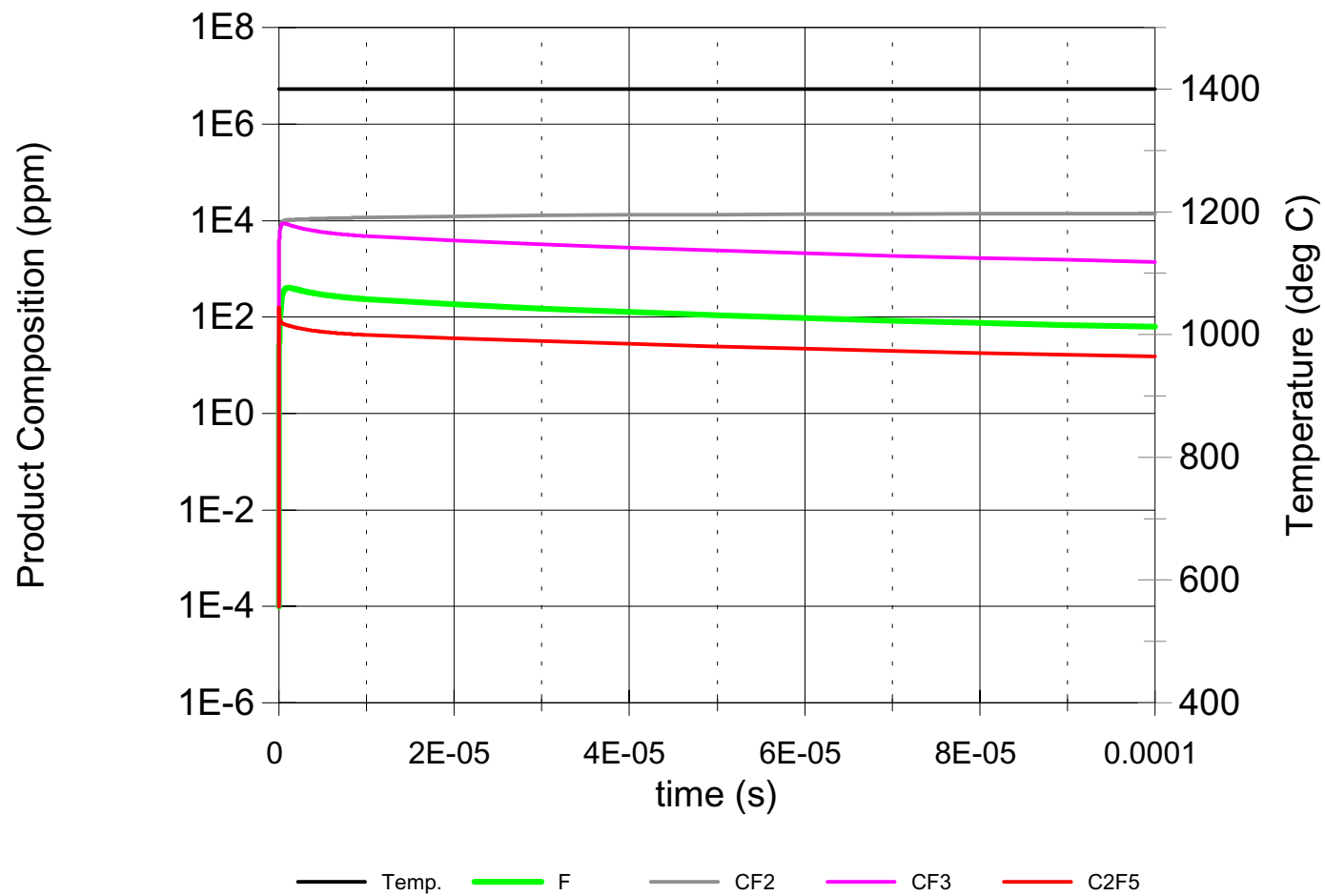


Fig. 2. Pyrolysis of 5000 ppm C_4F_{10} (radicals and oxidizer species only).

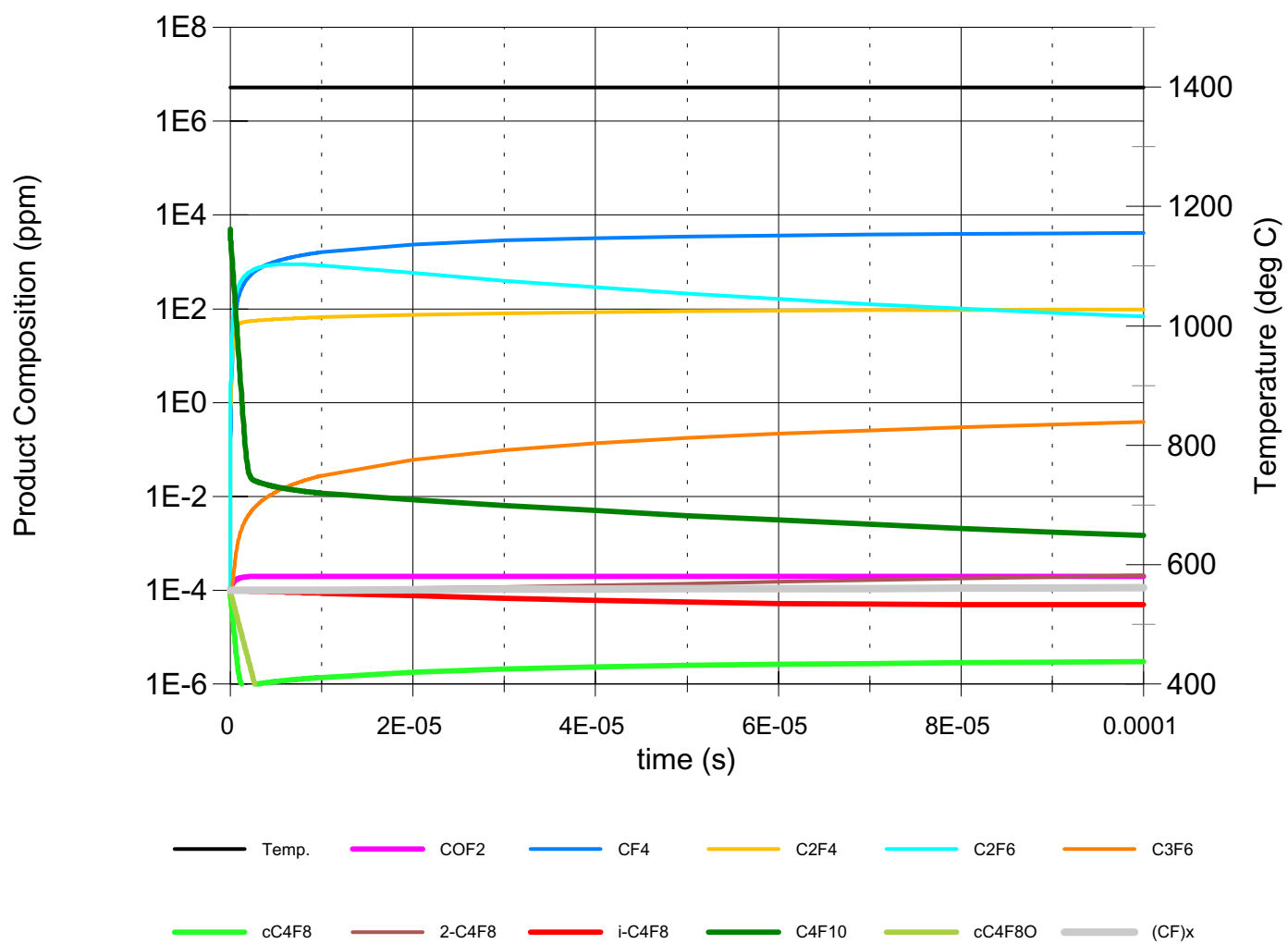


Fig. 3. Pyrolysis of 5000 ppm C_4F_{10} (stable C-containing species only).

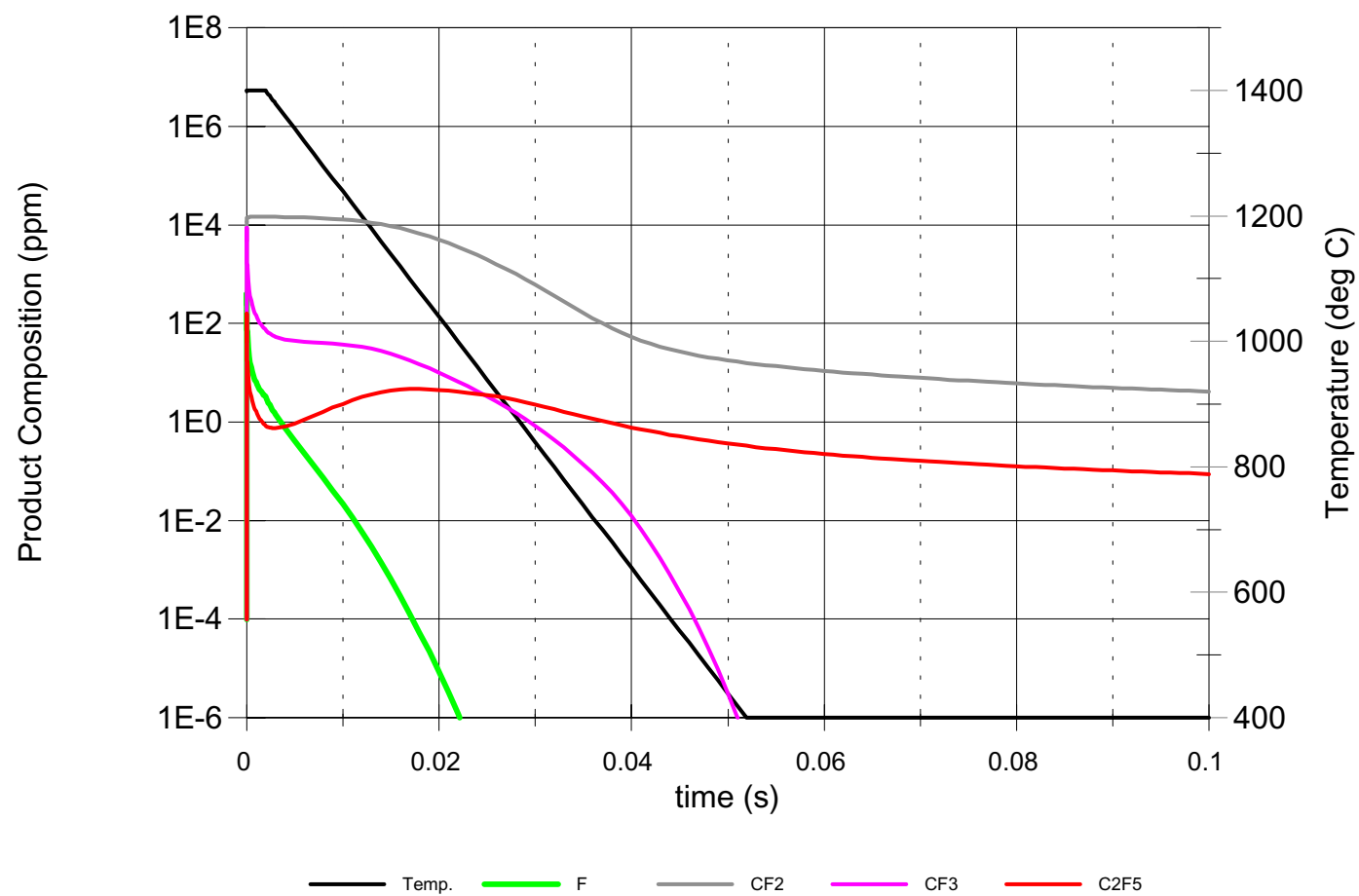


Fig. 4. Pyrolysis of 5000 ppm C_4F_{10} (radicals and oxidizer species only).

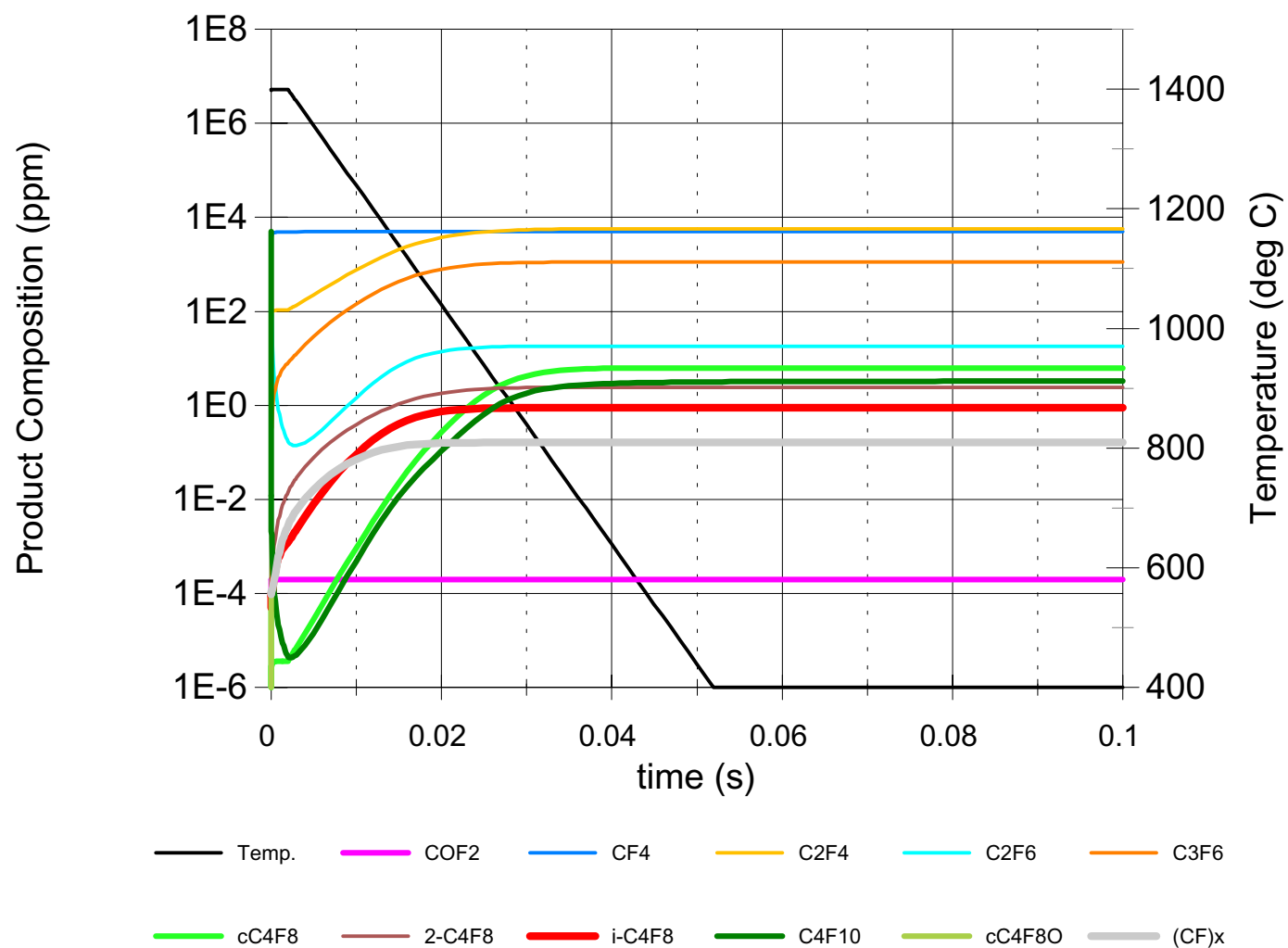


Fig. 5. Pyrolysis of 5000 ppm C₄F₁₀ (stable C-containing species only).

outcome only a little for the species of primary concern. For example, the earlier case, corresponding to the present 5000 ppm c-C₄F₈ pyrolysis case, was derived from a streamline located 10% radially outward from the center of the flame. It yielded 2.27 ppm PFIB in the earlier calculation (Trowbridge 1999a) versus the present result of 2.09 ppm.

3.4.3 Cases Including Oxygen Reactions

Addition of a reasonably complete set of combustion reactions (fuel, oxygen, etc.) to the pyrolysis model would require a great deal more work and was not planned as part of this project. Since, however, for the higher concentrations of the coolants, the PFIB production predicted from the pure pyrolysis cases may be too high to dismiss, some effort was spent in assessing the effect of oxygen on fluorocarbon pyrolysis. The reaction set used for the oxygen runs was discussed in Sect. 3.2. Results for the cases run are summarized in Table 4 and provided in greater detail in Appendix A, Table A.2.

The inclusion of the many additional species and reactions in these high-temperature cases resulted in extremely slow run times (days in many cases and weeks in a few cases). After examining the results from early partially complete runs, it became evident that most of the major net chemical activity appeared to be largely over within about 20 ms of simulation time. With faster computing resources, all these cases were taken to 52 ms of simulation time, the time at which the gas had cooled to its final temperature. At that point it was clear that no further significant changes in toxic species concentrations could occur. One case (2% C₄F₁₀ plus 2.7% O₂) was taken to a simulation time of 52 ms. While it did not reach the arbitrary 0.1 s originally intended duration of the run, the end time represented a fully cooled system, and its results were consistent with the remainder of the cases examined at 52 ms. For consistency, results taken at 52 ms are reported for all runs.

To illustrate the effect of oxygen addition on the course of pyrolysis, results from the 2.7% O₂ + 2% c-C₄F₈O case are plotted in Figs. 6 through 9. Figures 6 and 7 show the first 0.1 ms of the simulation, all of which occurs at the peak temperature. Cyclo! C₄F₈O steadily decomposes early in this period. Its various fragments lead to the rapid production of other fluorocarbons (in particular, CF₂, CF₃, C₂F₄, C₃F₆, C₂F₆, and CF₄) and oxidation products, including CO₂, CO, and COF₂. Oxygen is slowly consumed during this period. Several of these species rise to a peak and then decline as more and more carbon is sequestered in the most stable products (CF₄, CO, and CO₂). In particular, PFIB rises early (while CF₂ and C₃F₆ are present in high concentration) and then declines as C₃F₆ is consumed.

Figures 8 and 9 show the full computed course of the reaction. Major products nearly reach their final concentrations very early in the course of the reaction, and significant changes cease as the gas cools below about 1300°C. Radical species have all fallen below 1 ppm by the time the gas

Table 4. Summary of results for propane burner – oxygen reactions included

(all quantities are in units of mole ppm unless otherwise indicated)

Coolant	Rate set	Initial		Final			Other Major Product Gases	Notes ^a
		Coolant	Oxygen	PFIB	COF ₂ ^a	CO ^a		
c-C ₄ F ₈	Oxygen	5,000	27,000	<1 ppb	198	4,440	CF ₄ , CO ₂ , O ₂	<i>b</i>
C ₄ F ₁₀	Oxygen	5,000	27,000	<1 ppb	227	3,400	CF ₄ , CO ₂ , O ₂	<i>b</i>
c-C ₄ F ₈ O	Oxygen	5,000	27,000	<1 ppb	675	6,420	CF ₄ , CO ₂ , O ₂	<i>b</i>
c-C ₄ F ₈	Oxygen	20,000	27,000	0.16	1 ppb	17,500	CF ₄ , CO ₂ , C ₂ F ₄ , C ₃ F ₆	<i>b</i>
C ₄ F ₁₀	Oxygen	20,000	27,000	<1 ppb	69.7	13,500	CF ₄ , CO ₂ , O ₂	<i>b</i>
c-C ₄ F ₈ O	Oxygen	20,000	27,000	<1 ppb	323	27,300	CF ₄ , CO ₂ , O ₂	<i>b</i>
c-C ₄ F ₈	Oxygen	20,000	27,000	35.3	<1 ppb	6,870	C ₂ F ₄ , C ₃ F ₆ , CF ₄ , CO ₂ ,	<i>b</i>
C ₄ F ₁₀	Oxygen	20,000	5,000	15.5	<1 ppb	6,340	CF ₄ , C ₂ F ₄ , C ₃ F ₆ , CO ₂	<i>b</i>
c-C ₄ F ₈ O	Oxygen	20,000	5,000	4.7	<1 ppb	22,900	CF ₄ , C ₂ F ₄ , CO ₂ , C ₃ F ₆	<i>b</i>

^a Production rates for CO and COF₂ provide an indication of the likely ratio of these products but are unlikely to be quantitatively realistic, as

combustion products of the propane fuel are not included.

^b Total duration of run was 0.052 s .

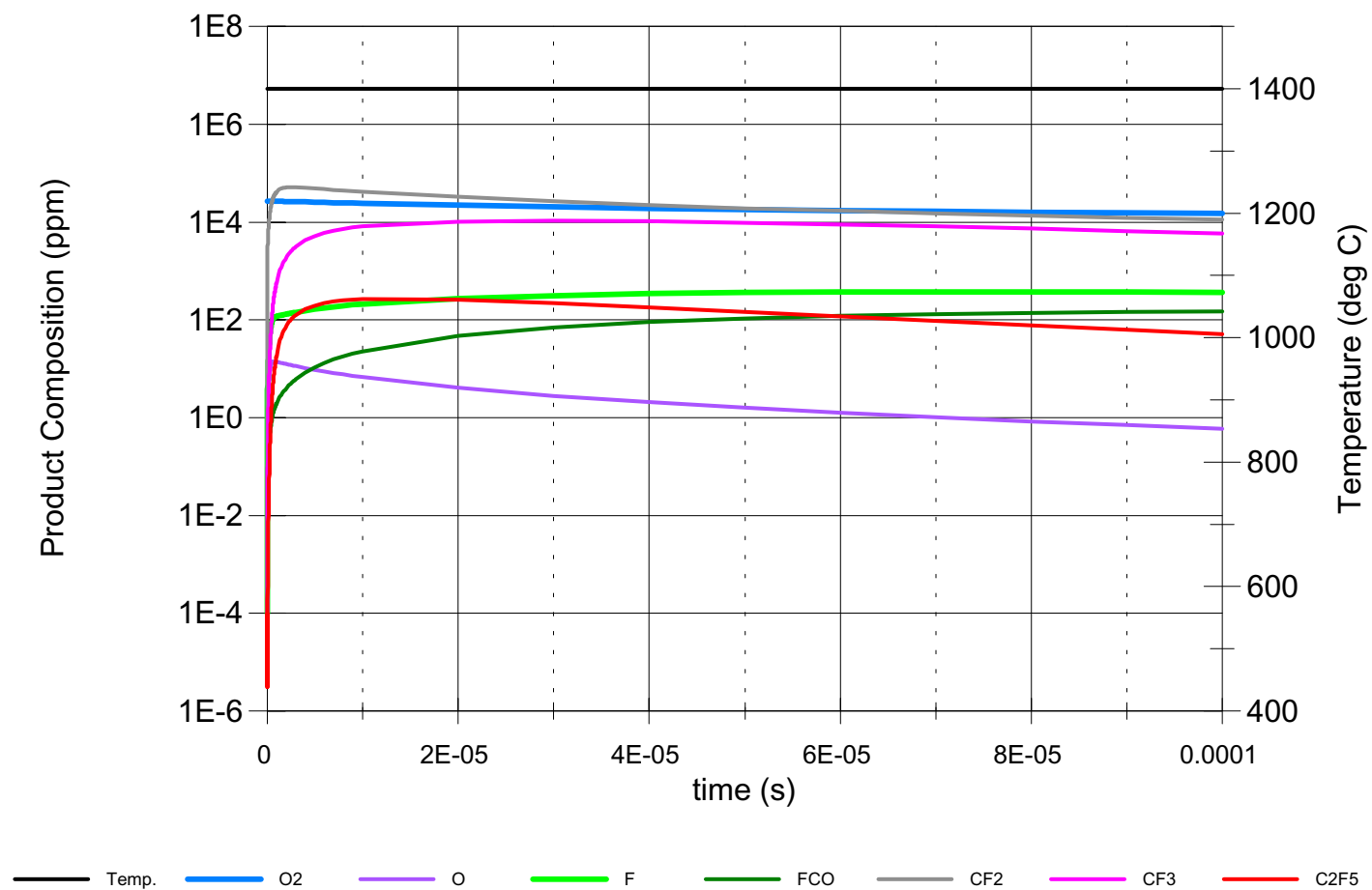


Fig. 6. Reaction of 2% c-C₄F₈O + 2.7% O₂ (radicals and oxidizer species only).

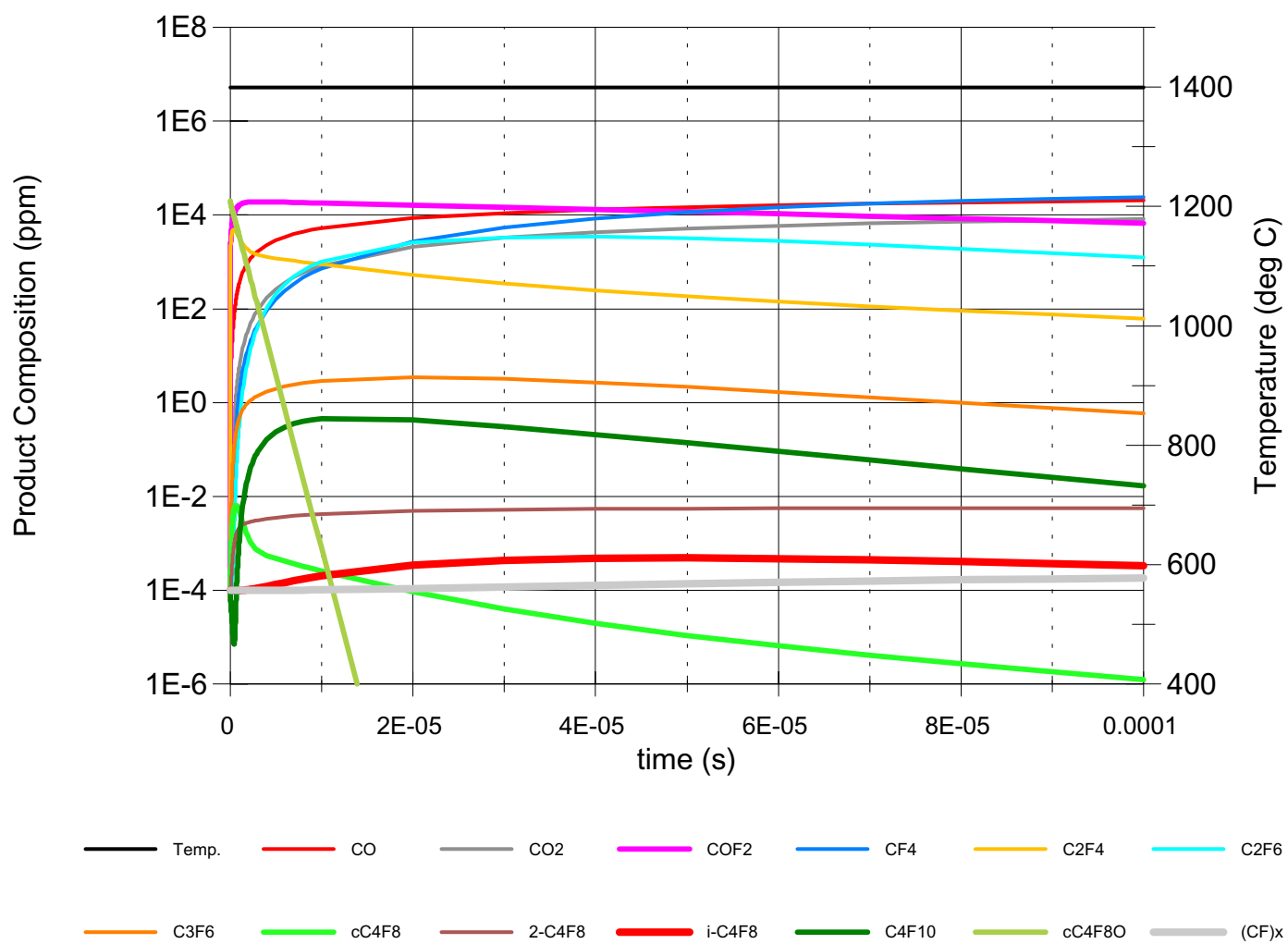


Fig. 7. Reaction of 2% c-C₄F₈O + 2.7% O₂ (stable C-containing species only).

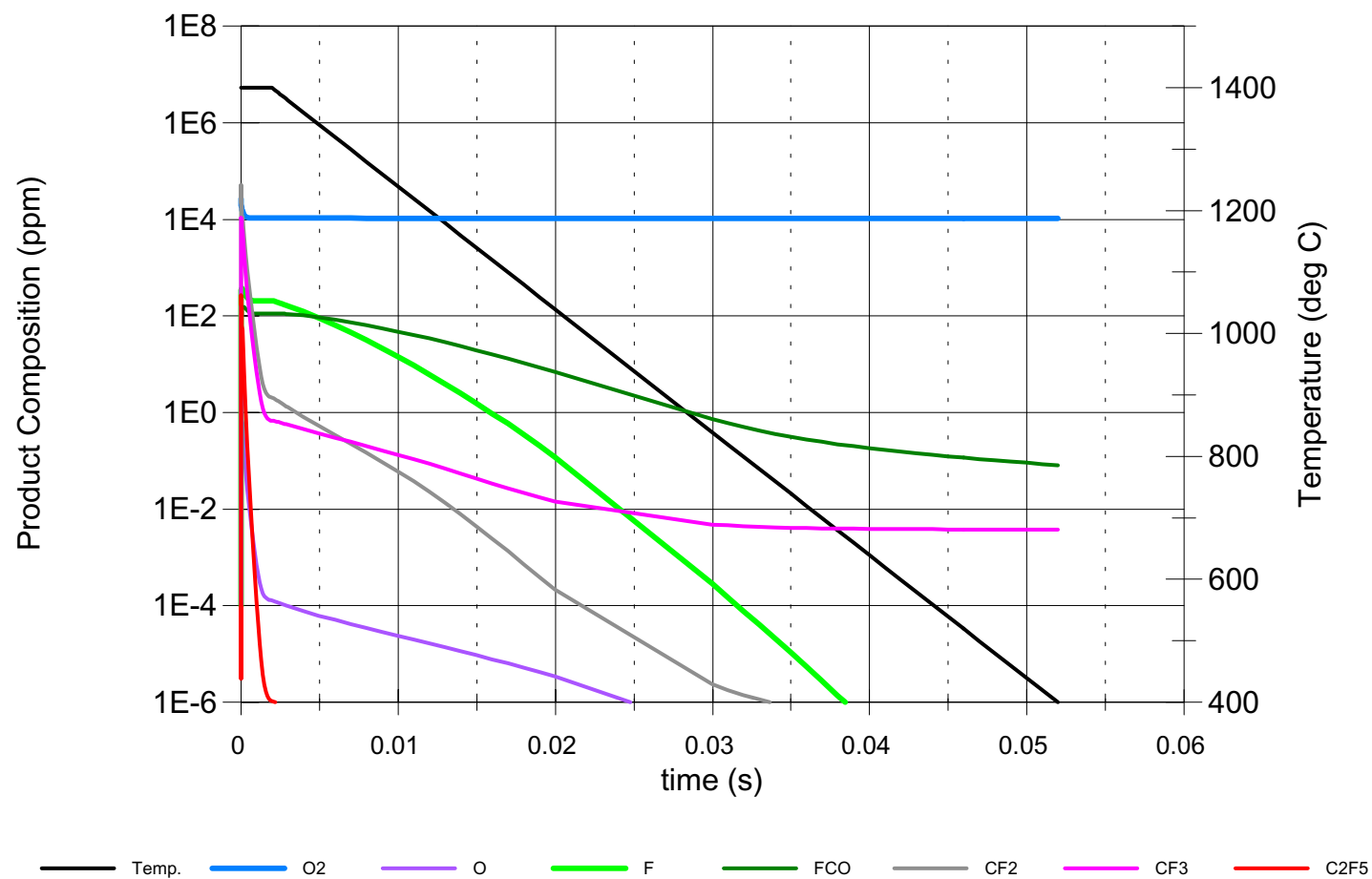


Fig. 8. Reaction of 2% c-C₄F₈O + 2.7% O₂ (radicals and oxidizer species only).

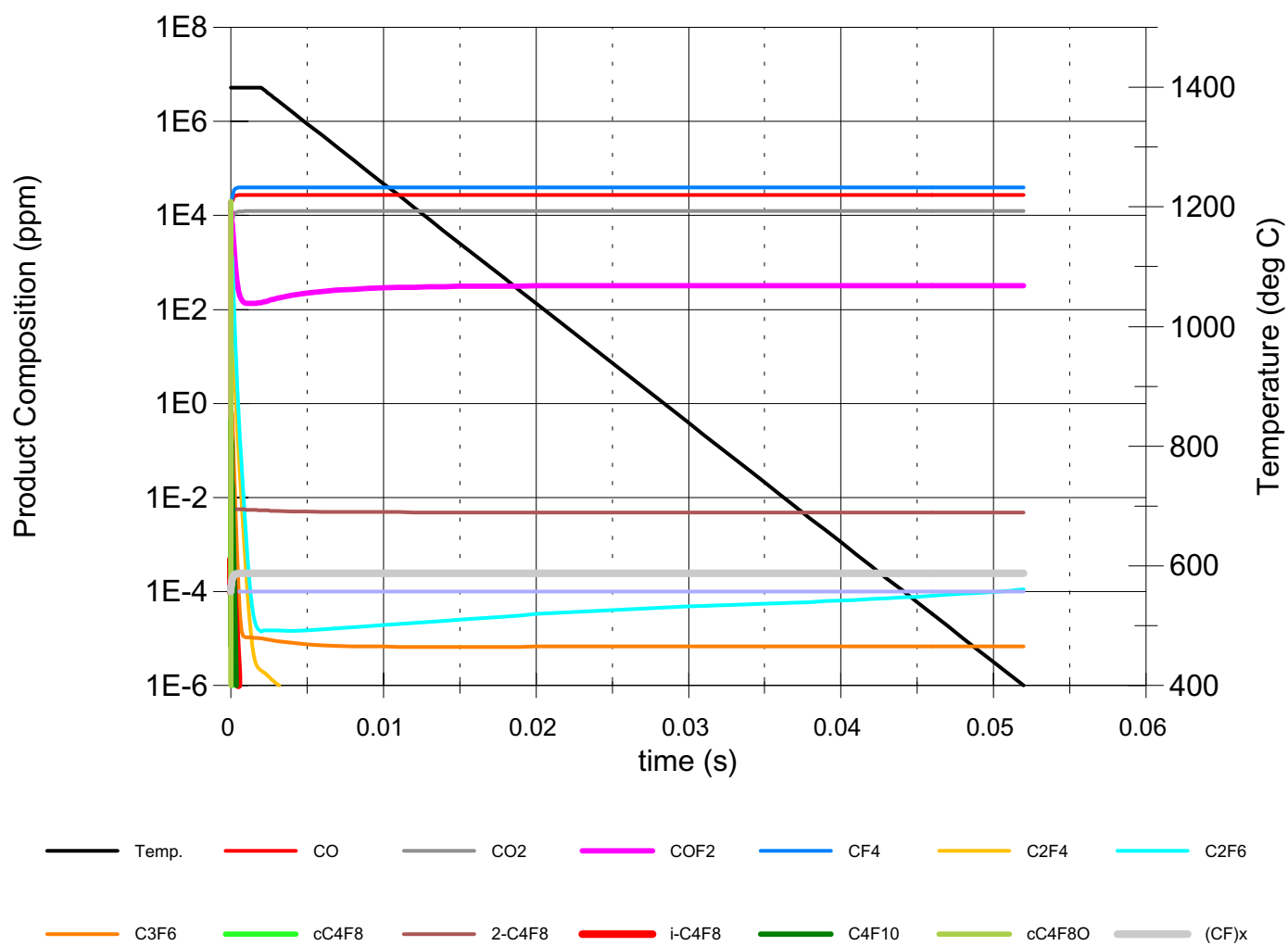


Fig. 9. Reaction of 2% c-C₄F₈O + 2.7% O₂ (stable C-containing species only).

has cooled below about 900°C.

In this particular case, the rate and mechanism of decomposition of c-C₄F₈O were not available from any theoretical or experimental source and had to be estimated. It is evident from the behavior of the calculation that the result is not sensitive to that rate or mechanism. If the rate were ten or even a hundred times slower or faster, decomposition would still have been essentially complete while the gas was still at its maximum temperature. Similarly, if the reaction products were other than the ones postulated (e.g., COF₂ and C₃F₆ rather than the postulated COF₂, CF₂ and C₂F₄), they would have rapidly equilibrated to the high-temperature composition calculated.

A variable difficult to quantify in the oxygen scenarios is the appropriate value for the initial oxygen content. In air, oxygen is on the order of 20%, but after combustion, it will be much lower, or even virtually absent, depending on the details of the fuel-air ratio, temperature, dwell time, etc. In these calculations, the fuel-air reaction is idealized as simply providing an elevated temperature environment, without including the chemical species that might be present due to the fuel. A value for oxygen of 2.7% was chosen for the base cases in this series. This represents the oxygen that would be unconsumed by a propane-air flame that is slightly fuel-lean but not so much as to greatly affect the peak flame temperature. In effect, this assumption allows combustion of the fuel to go to completion before any interaction of coolant with O₂ is permitted and also of prevention of interaction of combustion products (notably CO and H₂O, plus high-temperature radicals) with the coolant. These assumptions are not realistic but certainly should minimize the overall influence of O₂ and should overestimate the production of PFIB.

Two cases were run using a lower initial coolant concentration (5,000 ppm). A 2.7% O₂ concentration is more than enough to represent a substantial excess at this level. The remainder of the cases (including the one discussed previously for purposes of illustration) used an initial coolant concentration of 2% (20,000 ppm). Nominally, 2.7% O₂ would be inadequate to completely combust 2% c-C₄F₈, leading to the possibility of complete consumption of oxygen and the potential for formation of PFIB from the surviving CF₂. Observations from the pyrolysis kinetic runs, however, suggest that the following overall reaction will dominate:



where CF₂ is the result of fragmentation of the coolant and the O represents oxygen available from either O₂ or as part of the fluoroether. This is only an approximation, as other species appeared in the pyrolysis cases, but it indicates that in general, at least when there is a shortage of oxygen, that one oxygen atom can remove two CF₂ groups from availability (availability to produce PFIB, that is) rather than only one, which would be the case if CO₂ were the primary

reaction product. Thus, 2.7% oxygen should nominally be sufficient to remove the “available CF_2 ” from 2.7% c- C_4F_8 , 3.6% C_4F_{10} , or 5.4% c- $\text{C}_4\text{F}_8\text{O}$. That observation derives from the pyrolysis runs in which a very low effective concentration of oxygen (i.e., that in c- $\text{C}_4\text{F}_8\text{O}$) was present. The trend begins to weaken when higher oxygen concentrations are present. In the kinetic calculations, oxygen (when available in excess) formed considerable CO_2 in addition to CO and small concentrations of COF_2 . The formation of CO_2 was sufficient in one case (2.7% O_2 + 2% c- C_4F_8) to result in complete consumption of O_2 and the appearance of a trace amount of PFIB in the product mix.

Depending on the fuel-air mix, the available post-burn concentration might be higher or lower than 2.7%. The flame in the burner tip is predominantly a premixed flame (i.e., the fuel and oxidizer are mixed prior to burning). However, the structure of the tip provides a good supply of additional air at the edge of the flame that can diffuse into the flame if there is an oxygen deficit. Overall, an oxygen-poor environment is not likely. Nevertheless, to explore this, two cases were run with only 5000 ppm initial O_2 . These resulted in complete consumption of O_2 and the formation of unsaturated fluorocarbons and, consequently, of low levels of PFIB.

3.4.4 Propane Burner -- Summary and Conclusions

The PFIB generation predicted in these pure pyrolysis and pyrolysis/oxidation calculations ranges from nil to fairly small but is not in all cases completely trivial. Due apparently to the limited residence time at temperatures at which PFIB precursors (CF_2 and C_3F_6) are simultaneously stable, the very high concentrations reported in some pyrolytic synthesis techniques do not appear, even in the pure pyrolysis cases. Interactions with other combustion products, had they been considered, would reduce PFIB concentrations to levels much lower than those predicted here. In the presence of oxygen, PFIB formation is suppressed at these temperatures in favor of CF_4 formation, other saturated fluorocarbons, and the oxygenated species CO, COF_2 , and CO_2 . These cases are a step closer to the reality of reaction in a flame environment but are by no means a true reflection of that environment. The additional carbon- and hydrogen-containing species inherent in the propane-air combustion mixture would certainly be intimately involved in the reaction system. In these simulations, when oxygen is in excess, most of the fluorine initially present in the fluorocarbon appears as saturated fluorocarbons, notably CF_4 . Based on the NIST HFC work (Linteris 1995), one would expect that a major proportion of that fluorine to appear as HF. Certainly, any fluorine appearing in COF_2 would be hydrolyzed to HF and CO or CO_2 , but probably much of the fluorine appearing as stable fluorocarbons in these kinetic simulations would be diverted toward HF formation were hydrogen-containing species and reactions included. The kinetics results presented here would suggest that the environment most likely to produce PFIB will involve oxygen-depletion, a high concentration of coolant, and long contact times at temperatures in the range of 700 to 1000°C.

If the PFIB formation rates predicted here give cause for concern, then it would be advisable to experimentally evaluate the system. Of the many factors that were not taken into account in this modeling study, most will tend to reduce PFIB production. Consequently, an experimental study would have a good chance of demonstrating that production levels are in fact safe in this propane burner environment even if the concentrations predicted in these kinetic studies are interpreted as excessive.

This analysis has concentrated on the fate of $c\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8\text{O}$, and C_4F_{10} in a flame environment, but it is quite likely that similar results would have been obtained were the same analysis done with CFC-114 as the coolant. The C-Cl bond is weaker than the C-F bond, so it would tend to dissociate more readily than C-F bonds. At flame temperatures, CFC-114 very likely would decompose largely to C_2F_4 and CF_2 . As the gas cools, a similar mix of products should form, although with the addition of HCl and various chlorine-containing compounds.

Tables A.1 and A.2 in Appendix A give output concentrations of all product species. To define a volumetric source term from the typical propane burner, these concentrations should be multiplied by the approximate gas flow into the burner. This was estimated as being approximately 218 std cm^3/s for a typical fuel and air flow. This is not adjusted for the minor changes in the number of moles of gas leaving as opposed to entering the flame (that change, only a few percent, is less than the variability of gas flows from one operation to the next).

3.5 METAL-INERT GAS WELDING SCENARIOS

The second arena in which coolant vapor may be exposed to high-temperatures is in welding, especially the welding of coolant system components. Here, the concern is that residual levels of coolant in the ambient air could be heated and decompose. The type of welding under consideration is termed MIG welding. It is a variety of arc welding in which an inert cover gas (usually a mixture of argon and carbon dioxide) floods the region being welded, preventing oxygen in the air from reaching and reacting with the hot metal. Two basic environments will be considered – the weld-side environment (in which coolant-bearing air mixes with heated cover gas) and the trans-weld environment (in which coolant-bearing air is heated by the hot metal directly opposite the weld).

3.5.1 Trans-Weld Cases

Since this scenario is primarily one of heating ambient air, oxygen was considered in most of the runs, with its initial value set at 20% by volume (200,000 ppm). A few cases were run in which

no initial oxygen was present (simulating, say, a coolant pipe that had been purged with an inert gas such as nitrogen, rather than being open to or purged with air). Since high coolant levels lead to higher PFIB production, the initial coolant level was considered to be 2% (20,000 ppm) in all runs. This was the highest coolant level discussed during project planning, but inside coolant piping, much higher levels are possible, so the results of this analysis may not be bounding.

Kinetics model results were computed using the same reaction set as that used in the oxygen burner cases. Three main variables were explored. First was the choice of coolant. Second, the peak temperature was varied over a considerable range. Trans-weld peak temperatures are likely to be at the low end of the temperature range explored (perhaps 450 to 700°C), but values up to 1250°C were used. Finally, in a few cases, the effect of absence of oxygen was explored.

The results of these runs are summarized in Tables 5 (oxygen cases) and 6 (anaerobic cases); complete results are listed in Tables A.3 and A.4. In no case involving oxygen was PFIB produced; rather, the tendency was for it to be destroyed. Only for runs at 700°C and above was significant destruction of coolant and formation of reaction products predicted. The 700°C cases represented the transition between nonreactivity and complete destruction of the coolants. In the 700°C runs, approximately one third of the initial $c\text{-C}_4\text{F}_8$ and C_4F_{10} and 84% of the initial $c\text{-C}_4\text{F}_8\text{O}$ are predicted to survive. The apparent higher survivability of $c\text{-C}_4\text{F}_8\text{O}$ is due solely to the rate constant parameters for its decomposition reaction. These were estimated and may not be quantitatively correct. Reaction products of the decomposed coolants consist largely of CF_4 , C_2F_6 , CO_2 , and COF_2 .

Peak temperatures of 1000°C result in complete conversion of any of these coolants to CF_4 , CO_2 , and COF_2 . The 1250°C peak temperature runs were very slow to execute and were run for a simulation time of only 1 s. At that time, the gas was still at high-temperature. In addition to the CF_4 , CO_2 , and COF_2 that we expect from the 1000°C cases, numerous high-temperature species are present (e.g., F, FCO), as is CO.

The large excess of oxygen in these scenarios suppressed the formation of CO and unsaturated fluorocarbons, including PFIB. All these species had a propensity to be destroyed rather than formed under the conditions investigated in these cases.

The most realistic peak temperatures are probably in the range of 400 to 500°C, not the higher temperatures (which are, incidentally, incandescent temperatures). The 500°C case resulted in coolant destruction of about a half a ppm (and one-tenth that for $c\text{-C}_4\text{F}_8\text{O}$), no PFIB or CO production, and formation of 0.1 to 1 ppm COF_2 . These concentrations would form in a volume of gas of the general size of the hottest region of metal, that is perhaps a few cubic centimeters. To convert this to a production source term, consider that approximately 1 std cm^3 of gas

Table 5. Summary of results for MIG Welding –Trans-weld cases
(all quantities in units of mole ppm unless otherwise indicated)

Coolant	Peak T (°C)	Initial		Final			Other major product gases	Notes
		Coolant	Oxygen	PFIB	COF ₂	CO		
c-C ₄ F ₈	400	20,000	200,000	<1 ppb	1 ppb	<1 ppb		
C ₄ F ₁₀	400	20,000	200,000	<1 ppb	2 ppb	<1 ppb		
c-C ₄ F ₈ O	400	20,000	200,000	<1 ppb	1 ppb	<1 ppb		
c-C ₄ F ₈	450	20,000	200,000	<1 ppb	25 ppb	<1 ppb		
C ₄ F ₁₀	450	20,000	200,000	<1 ppb	48 ppb	<1 ppb		
c-C ₄ F ₈ O	450	20,000	200,000	<1 ppb	4 ppb	<1 ppb		
c-C ₄ F ₈	500	20,000	200,000	<1 ppb	0.6	<1 ppb	CF ₄ , CO ₂	
C ₄ F ₁₀	500	20,000	200,000	<1 ppb	1.3	<1 ppb	CF ₄	
c-C ₄ F ₈ O	500	20,000	200,000	<1 ppb	0.1	<1 ppb	CF ₄	
c-C ₄ F ₈	700	20,000	200,000	<1 ppb	16,000	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	
C ₄ F ₁₀	700	20,000	200,000	<1 ppb	18,000	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	
c-C ₄ F ₈ O	700	20,000	200,000	<1 ppb	6,000	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	
c-C ₄ F ₈	1000	20,000	200,000	<1 ppb	14,000	<1 ppb	CF ₄ , CO ₂	
C ₄ F ₁₀	1000	20,000	200,000	<1 ppb	14,000	<1 ppb	CF ₄ , CO ₂	
c-C ₄ F ₈ O	1000	20,000	200,000	<1 ppb	28,000	<1 ppb	CF ₄ , CO ₂	
c-C ₄ F ₈	1200	20,000	200,000	<1 ppb	11,000	680	CF ₄ , CO ₂	<i>a</i>
C ₄ F ₁₀	1200	20,000	200,000	<1 ppb	11,000	520	CF ₄ , CO ₂	<i>a</i>
c-C ₄ F ₈ O	1250	20,000	200,000	<1 ppb	23,000	890	CF ₄ , CO ₂	<i>a</i>

^a Run terminated at 1 s

Table 6. Summary of results for MIG-welding – Anaerobic trans-weld cases

(all quantities in units of mole ppm unless otherwise indicated)

Coolant	Peak T (°C)	Initial		Final			Other Major Product Gases	Notes
		Coolant	Oxygen	PFIB	COF ₂	CO		
c-C ₄ F ₈	500	20,000	0	<1 ppb	n/a	n/a		
C ₄ F ₁₀	500	20,000	0	<1 ppb	n/a	n/a		
c-C ₄ F ₈ O	500	20,000	0	<1 ppb	56 ppb	<1 ppb		
c-C ₄ F ₈	700	20,000	0	0.5	n/a	n/a	C ₂ F ₄ , C ₃ F ₆	
C ₄ F ₁₀	700	20,000	0	5 ppb	n/a	n/a	C ₂ F ₄ , C ₂ F ₆ , C ₃ F ₆	
c-C ₄ F ₈ O	700	20,000	0	0.03	3,100	8	C ₂ F ₄ , C ₃ F ₆	
c-C ₄ F ₈	1000	20,000	0	143	n/a	n/a	C ₂ F ₆ , C ₃ F ₆ , 2-C ₄ F ₈ , (CF) _n	
C ₄ F ₁₀	1000	20,000	0	60	n/a	n/a	C ₂ F ₆ , C ₃ F ₆ , 2-C ₄ F ₈ , (CF) _n	
c-C ₄ F ₈ O	1000	20,000	0	18	<1 ppb	20,000	C ₂ F ₆ , C ₃ F ₆ , (CF) _n	<i>a</i>

^a Run duration terminated at 5 s

(occupying 3-cm³ volume) produces 1 ppm COF₂ in 1 min, or about 10⁻⁶ std cm³ /min. Roughly speaking, then, 1 ppm produced (as listed in Table 5) corresponds to 10⁻⁶ std cm³ /min of that material produced.

To bound PFIB production, runs were made at three peak temperatures (500, 700, and 1000°C) under anaerobic conditions (i.e., with no oxygen). These cases might depict the situation on the inside of piping which had been purged with an inert gas (e.g., dry nitrogen) rather than air. The first case used a peak temperature of 500°C and thus can be considered the most plausible based on the temperature information available. This case produced no PFIB and only slight coolant decomposition, the primary product for all coolants being C₂F₄. The temperature was not high enough for the precursors of PFIB to form in quantity in this case. The second set of pyrolysis cases used a maximum temperature of 700°C. About half of the initial c-C₄F₈ was pyrolyzed, producing largely C₂F₄ and C₃F₆, but also 0.4 ppm PFIB. Predicted decomposition of C₄F₁₀ and c-C₄F₈O were about 8% and 16%, respectively. The main products were C₂F₄, C₂F₆, C₃F₆ and (for c-C₄F₈O) COF₂. About 0.5 ppm PFIB was predicted for the c-C₄F₈ case and much less for the other two coolants. The final set of cases used a peak temperature of 1000°C. This case resulted in near-complete decomposition of all the coolants and the formation of large quantities of various unsaturated fluorocarbons, mostly C₂F₄ and C₃F₆, but including about 140 ppm PFIB in the case of c-C₄F₈ and 60 ppm PFIB for c-C₄F₁₀. The c-C₄F₈O case was one that ran extremely slowly and had to be terminated at a simulation time of 5 s, rather than going through the full 30s cool-down phase of the time-temperature profile. Consequently, its product mix included many high-temperature species. PFIB formation at 5 s was at 18 ppm and slightly rising. Between 5 and 30 s, the C₄F₁₀ run behaved similarly, with its PFIB concentration increasing 33%. A similar rise for c-C₄F₈O would have yielded a final PFIB concentration of about 24 ppm.

Except for the presence of oxygen, this trans-weld time-temperature environment most closely resembles the conditions conducive to formation of PFIB (lower temperatures and longer contact times). This condition is, however, apparently not the common practice. Furthermore, personnel are isolated from the immediate vicinity of this environment.

At normal humidity levels, the moisture content of air is on the order of 1 to 3% by volume, which is sufficient to consume the COF₂ listed in any of these runs, and produce a corresponding quantity of HF.

It may be helpful to relate these temperatures to common experience. Metal will begin to glow dull red at about 600°C. It glows cherry red at 900°C, then orange at about 1000°C, and yellow at about 1100°C (Lange 1964). Temperatures at which there is significant coolant decomposition will tend to be ones where the metal surface in question is visibly glowing and, of course, where coolant vapor can contact those surfaces.

The general conclusion to be drawn from these cases is that, within the limits of the available information and of the kinetics calculations, at reasonable temperatures, little or no PFIB should be produced in air from this environment. It should be noted that the highest concentration coolant considered was 2%. Much higher concentrations (up to pure coolant vapor) could occur inside unpurged systems.

3.5.2 Weld-Side Cases

The situation on the welded side of a MIG weld is the hardest to physically define in a convincing manner because the cover gas, intended to prevent oxygen from reaching the welded region, will also keep coolant from the hottest region (which must be above the melting point of iron at 1535°C). The gas flow used is on the order of 840 std L/h, so the cover gas near the weld will be moving at a velocity on the order of a meter per second. No meaningful penetration of ambient air to the molten welded region or the arc will occur under these conditions – if it did, the cover gas would not be fulfilling its function. The gases departing the weld region will be hot, however, and eventually air containing oxygen and coolant will mix with this departing cover gas. Since the coolant is presumed to be in the air and neither oxygen nor coolant are present in the cover gas, a wide range of compositions may exist. The ratio of coolant to oxygen, however, should be roughly fixed. Because the coolant molecules are larger and heavier than O₂, their diffusion into the hot inert gas will be slower than that of O₂, which could lead to some slight variation in this ratio. The main effect, however, will be simple mixing of the (perhaps hot) cover gas with the cold air/coolant mixture. The hottest gas, considered simply on a dilution basis, would contain the smallest air/coolant fraction.

A series of cases was defined using a very wide range of temperatures to span this environment. Rather than explore a large multidimensional parameter space, a fixed composition (with a probably unrealistically large fraction of air/coolant mix, namely 50%) was chosen. Coolant is taken to be 1% by volume, and oxygen, 10% by volume (i.e., originally from a mix of 2% coolant in air). This ratio will always provide excess oxygen beyond what is needed to fully combust the coolant.

The time-vs-temperature profile for these cases was somewhat arbitrarily defined but is based on gas flow rates and dimensions of the weld and gas flow. The details are discussed above in Sect. 3.3.2.

A summary of the results of these runs is listed in Table 7 and the detailed results are contained in Table A.5. At 700°C, less than 1% of the coolant fails to survive the environment, but for runs at 1000 and 1500°C, the coolants are completely consumed. In no case is PFIB formed; rather, the

Table 7. Summary of results for MIG-welding – Weld-side cases

(all quantities in units of mole ppm unless otherwise indicated)

Coolant	Peak T (°C)	Initial			Final		Other major product gases	Notes
		Coolant	Oxygen	PFIB	COF ₂	CO		
c-C ₄ F ₈	700	10,000	100,000	<1 ppb	41	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	<i>a</i>
C ₄ F ₁₀	700	10,000	100,000	<1 ppb	48	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	<i>a</i>
c-C ₄ F ₈ O	700	10,000	100,000	<1 ppb	120	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	<i>a</i>
c-C ₄ F ₈	1000	10,000	100,000	<1 ppb	5,660	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	
C ₄ F ₁₀	1000	10,000	100,000	<1 ppb	5,110	<1 ppb	CF ₄ , C ₂ F ₆ , CO ₂	
c-C ₄ F ₈ O	1000	10,000	100,000	<1 ppb	13,400	2.3	CF ₄ , C ₂ F ₆ , CO ₂	
c-C ₄ F ₈	1500	10,000	100,000	<1 ppb	2,070	6,320	CF ₄ , CO ₂	<i>b</i>
C ₄ F ₁₀	1500	10,000	100,000	<1 ppb	2,140	4,430	CF ₄ , CO ₂	<i>b</i>
c-C ₄ F ₈ O	1500	10,000	100,000	<1 ppb	3,940	8,800	CF ₄ , CO ₂	<i>b</i>

^a Less than 1% decomposition of coolant predicted^b Run terminated at 0.3 s

tendency is for it to be destroyed. The reaction product mix predicted is fairly simple. In all cases, oxygen was present in large excess and appeared to suppress the formation of unsaturated fluorocarbon products. At lower temperatures, the predominant product gases are CF_4 , C_2F_6 , CO_2 , and COF_2 . At the highest temperature run (an unrealistically high 1500°C , nearly the melting point of iron), C_2F_6 disappears and COF_2 diminishes in favor of additional CF_4 and CO .

The most realistic thermal environment is likely to be represented by the lowest peak temperature examined (if not lower still), and therefore little decomposition of coolant is to be expected in this scenario. Because establishing a convincing mass flow value for any of these cases is quite difficult, no attempt was made to deduce production terms for COF_2 and CO . Obviously, the concentrations derived from this model would apply to a gas flow that is a small fraction of the total cover gas flow (which is about 14 std L/min), but how small a fraction is uncertain. To accurately model the highly variable geometric, thermal, and mass transport environment involved in the welding operation would be a complicated endeavor. Far more convincing would be to physically monitor the gas departing a MIG welding operation for HF or other reactive halogens (e.g., COF_2) and for CO .

3.5.3 Conclusions Regarding Weld Scenarios

In neither weld scenario set was PFIB formation predicted when the presence of oxygen was considered. On both the side of the material being welded and the side opposite the weld, coolant will apparently be present only when mixed with air. Oxygen depletion is not the uncertainty it was in the propane flame case. Only if welding occurred opposite a container with very high coolant concentrations (a situation outside the realm analyzed here) or one purged with an inert gas would PFIB formation be predicted. If extensive decomposition of the coolant occurs in the presence of oxygen, the major toxic species of concern would be COF_2 and HF, which have similar toxicity levels.

4. CONCLUSIONS

Chemical kinetics calculations were performed to estimate the decomposition and oxidation behavior of the three candidate coolants $c\text{-C}_4\text{F}_8$, C_4F_{10} , and $c\text{-C}_4\text{F}_8\text{O}$. Two high-temperature operations were simulated. These environments, the propane flame leak test device and MIG welding, represent conditions that credibly might result in decomposition of the coolant vapors. Some of the conditions examined produced little or no decomposition of the coolants (e.g., credible temperatures on the side of a metal piece opposite the location of a welding operation). The highest temperature scenarios were those simulating the propane flame and the higher temperature regions of a MIG-weld cover gas plume. In such conditions, any fluorocarbon coolant is predicted to rapidly decompose to light molecules and radicals. The set of high-temperature reaction fragments is identical in character for all three coolants, with minor variations in concentration due to the different chemical formulae of the parent coolants. Similarly the ultimate reaction products are the same in character but may differ somewhat quantitatively. As the gas cools, the fragments form stable species, a few of which may be hazardous. In the presence of sufficient O_2 , the kinetics modeling predicted no PFIB formation. The primary hazardous products predicted in the modeling are CO and COF_2 , to which would be added HF had hydrogen-containing species been considered.

Only for high-temperature, extended-duration anaerobic conditions is PFIB formation predicted. Such conditions do not appear to be among the credible scenarios examined. If such conditions were to be encountered, however, the kinetics calculations predict that $c\text{-C}_4\text{F}_8$ will produce somewhat more PFIB than the other two coolants. Of the three coolants, the fluoroether $\text{C}_4\text{F}_8\text{O}$ generally was predicted to produce more COF_2 than the other two coolants, due to the additional oxygen inherent in its chemical formula.

Indications from the literature suggest that PFIB formation most readily occurs within a restricted range of temperatures and requires relatively long-term contact (many seconds to hours). The presence of air and humidity tends to reduce or eliminate the formation of PFIB but will allow the formation of other toxic compounds such as HF, CO, and COF_2 . A flame environment seems to suppress formation of PFIB. The kinetics results point to the same conclusions. An anaerobic environment allows formation of PFIB within the proper temperature range. The proper temperature range is that which is hot enough for partial decomposition of fluorocarbons and formation of significant quantities of the two precursor species CF_2 and C_3F_6 but not so hot as to decompose C_3F_6 . Temperatures found in a flame environment are too high for significant formation of PFIB, however, and would tend to dissociate any PFIB previously present. Only on cooling can PFIB form. Additionally, nearby regions heated to the ideal temperature range might also form PFIB. The time-and-temperature combination in a flame environment is not particularly conducive to PFIB formation even ignoring the effect of oxygen and other combustion products.

While the kinetics and most chemical literature suggest that PFIB should not form in the presence of O_2 , there are two factors that point toward the possibility of PFIB formation. First, some descriptive chemistry literature indicated that PFIB was found in fluorocarbon polymer pyrolysis experiments involving air (although always at a lower level than in an inert gas environment). Conditions in these experiments were never sufficiently defined, however, to rule out the possibility of local oxygen depletion. This leads to the second point: in the operational scenarios examined here, an environment in which oxygen depletion might occur cannot be absolutely ruled out in the most extreme cases.

Although the decomposition or oxidation of CFC-114 was not specifically covered in either literature reports or in the kinetics modeling performed here, we note that closely related compounds (including HFCs, chlorofluorocarbons and bromofluorocarbons) all seem to thermally decompose to form products very similar to those of these three coolants. This suggests that the toxic fluorocarbon decomposition products of the CFC-114 would be quite similar to those of these fluorocarbons in similar environments.

More definitive results would require much more extensive kinetic analysis and would always be subject to the possibility of something important being overlooked or inaccurate rate information. Experimentation is a surer guide to reality, although it can rarely span all possible combinations of conditions. The trends and conclusions obtained from chemical reaction modeling appear generally favorable, but if definite confirmation is needed, experimentation ought to be performed. The kinetics and literature search can guide the experimental search toward those conditions most likely to be a problem. Specifically, conditions that should be most closely examined are those involving high concentrations of coolant, relatively long contact time in the ideal temperature range, and little or no oxygen or moisture.

Regarding the behavior of these three coolants upon cascade inleakage, the best guidance that can be given is the experimental observation that at conditions roughly simulating a cascade inleakage environment, none of these coolants showed evidence of reaction with UF_6 . Reactivity of all three coolants with F_2 , a considerably stronger fluorinating agent than UF_6 , was less than the minimal reactivity exhibited by the present coolant, CFC-114. No unique reaction products are likely in a cascade environment. Should coolants and fluorinating agents be inadvertently mixed, flammable or explosive gas mixtures could be created, but that is the case for C-114 as well.

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Appendix A

KINETICS MODEL RESULTS

The following tables contain the detailed results of the kinetics model cases discussed in the main text of this report. Several tables are presented, one for each general class of reaction scenario.

Some table entries may bear explanation. The “Scenario ID” is a computer filename series used for that particular case. The “final time” is the total duration of the run (in simulation time) for that particular case. The coolant used in that run is identified in the next row. The next two rows indicate the starting concentrations of coolant and oxygen, in mole parts per million (ppm). The remainder of the table (except for possible notes at the end) consists of final concentrations of all species, again in parts per million. To keep the tables in a common format, the structure is identical for all cases. Thus some listed species were not actually considered in certain runs. For example, pure pyrolysis of $\text{c-C}_4\text{F}_8$ or C_4F_{10} required no oxygen-containing species, and thus none of these species, nor reactions involving them, were actually considered in such runs. Their entries will read zero in the table, as will the entries for species which *were* considered, but whose final computed concentrations were less than half a part per million.

Table A.1. Initial conditions and final results for Propane Burner Scenarios (Anerobic Cases)

Scenario ID	Pyr318i	Pyr31Ai	PyrTHFu	Pyr318v	Pyr31Av	PyrTHFs	Pyr318t	Pyr31At	PyrTHFw
Final time	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Max T (°C)	1400	1400	1400	1400	1400	1400	1400	1400	1400
Coolant is...	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O
Initial Concentrations (ppm)									
Coolant	1000	1000	1000	5000	5000	5000	20000	20000	20000
O ₂	0	0	0	0	0	0	0	0	0
Final Concentrations (ppm)									
CF ₄	0.000	994.850	995.950	0.000	4978.100	4983.900	0.482	19911.00	19934.000
C ₂ F ₄	1869.700	1423.500	964.240	7068.900	5764.500	4192.100	13828.000	12635.00	10605.000
C ₂ F ₆	0.000	3.989	3.119	0.104	18.612	13.570	32.519	93.993	62.016
C ₃ F ₆	84.577	46.659	20.244	1928.700	1133.100	524.110	16964.000	11299.000	6135.300
c-C ₄ F ₈	0.570	0.315	0.134	9.687	6.305	3.214	39.527	32.733	22.692
2-C ₄ F ₈	0.065	0.029	0.010	5.622	2.460	0.800	221.330	100.030	34.877
i-C ₄ F ₈ (PFIB)	0.014	0.005	0.001	2.092	0.895	0.262	57.567	31.665	12.583
C ₄ F ₁₀	0.000	1.099	0.895	0.350	3.338	2.539	6.905	10.584	7.740
c-C ₄ F ₈ O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Solid (CF) _n	0.001	0.001	0.000	0.494	0.162	0.037	39.951	15.494	4.439
C / O Species	CO ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	COF ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	CO	0.000	0.000	1000.000	0.000	0.000	5000.000	0.000	20000.000
Oxygen	O ₂	0	0	0	0	0	0	0	0
Radicals	CF ₂	4.326	4.325	4.313	4.132	4.192	4.259	3.793	3.957
	CF ₃	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	C ₂ F ₅	0.003	0.088	0.088	0.081	0.089	0.089	0.090	0.090
	F	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	FCO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
	O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table A.2. Initial conditions and final results for Propane Burner Scenarios (Aerobic Cases)^a

Scenario ID	PyO318b	PyO31Ab	PyOTHFb	Py318A	PyO31Aa	PyOTHFa	PyO318c	PyO31Ac	PyOTHFc
Final time	0.052	0.052	0.052	0.052	0.052	0.052	0.052	0.052	0.052
Max T (°C)	1400	1400	1400	1400	1400	1400	1400	1400	1400
Coolant is...	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O
Initial Concentrations (ppm)									
Coolant	5000	5000	5000	20000	20000	20000	20000	20000	20000
O ₂	27000	27000	27000	27000	27000	27000	5000	5000	5000
Final Concentrations (ppm)									
CF ₄	9901.000	12386.000	9662.600	35689.000	49965.000	39839.000	8347.400	28095.000	26403.000
C ₂ F ₄	0.000	0.000	0.000	3665.300	0.000	0.000	12871.000	11053.000	8581.400
C ₂ F ₆	0.000	0.000	0.000	33.865	0.008	0.000	94.108	71.143	47.380
C ₃ F ₆	0.000	0.000	0.000	381.660	0.000	0.000	12153.000	7028.900	3238.900
c-C ₄ F ₈	0.000	0.000	0.000	2.421	0.000	0.000	34.017	24.744	14.563
2-C ₄ F ₈	0.001	0.000	0.000	0.536	0.002	0.005	114.200	43.938	12.280
i-C ₄ F ₈ (PFIB)	0.000	0.000	0.000	0.157	0.000	0.000	35.293	15.492	4.679
C ₄ F ₁₀	0.000	0.000	0.000	3.093	0.000	0.000	10.600	8.344	5.896
c-C ₄ F ₈ O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Solid (CF) _n	0.000	0.000	0.000	0.020	0.000	0.000	18.088	5.862	1.232
C / O Species	CO ₂	5458.100	3985.400	3247.700	18274.000	16417.000	12564.000	1565.800	1830.500
	COF ₂	198.250	227.250	675.110	0.001	69.732	323.050	0.000	0.000
	CO	4443.000	3400.900	6415.000	17452.000	13548.000	27274.000	6868.300	6339.000
Oxygen	O ₂	19221	21201	22706	0	3774	10636	0	0
Radicals	CF ₂	0.000	0.000	0.000	15.615	0.000	0.000	16.425	16.383
	CF ₃	0.000	0.000	0.000	0.000	0.032	0.004	0.000	0.000
	C ₂ F ₅	0.000	0.000	0.000	0.336	0.000	0.000	0.345	0.339
	F	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	FCO	0.081	0.081	0.086	0.000	0.077	0.083	0.000	0.000
	O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

^a Due to slow run times, all runs in this series were halted at 52 ms, the time at which the temperature profile first reached 400°C.

Table A.3. Initial conditions and final results for MIG Welding: Trans-Weld Scenarios (Aerobic Cases)

Part 1

Scenario ID		TWL318a	TWL31Aa	TWLTHFa	TWL318e	TWL31Ae	TWLTHFe	TWL318b	TWL31Ab	TWLTHFb
Final time		30	30	30	30	30	30	30	30	30
Max T (°C)		400	400	400	450	450	450	500	500	500
Coolant is...		c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O
Initial Concentrations (ppm)										
Coolant		20000	20000	20000	20000	20000	20000	20000	20000	20000
O ₂		200000	200000	200000	200000	200000	200000	200000	200000	200000
Final Concentrations (ppm)										
CF ₄		0.000	0.000	0.000	0.010	0.012	0.000	0.624	0.753	0.028
C ₂ F ₄		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₂ F ₆		0.000	0.000	0.000	0.001	0.001	0.000	0.024	0.024	0.000
C ₃ F ₆		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
c-C ₄ F ₈		20000.000	0.000	0.000	20000.000	0.000	0.000	19999.500	0.000	0.000
2-C ₄ F ₈		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
i-C ₄ F ₈ (PFIB)		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₄ F ₁₀		0.000	20000.000	0.000	0.000	20000.000	0.000	0.000	19999.400	0.000
c-C ₄ F ₈ O		0.000	0.000	20000.000	0.000	0.000	20000.000	0.000	0.000	19999.940
Solid (CF) _n		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C / O Species	CO ₂	0.001	0.001	0.001	0.025	0.010	0.003	0.716	0.277	0.089
	COF ₂	0.001	0.002	0.001	0.025	0.048	0.004	0.663	1.269	0.111
	CO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Oxygen	O ₂	200000	200000	200000	200000	200000	200000	200000	200000	200000
Radicals	CF ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	CF ₃	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	C ₂ F ₅	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	F	0.001	0.001	0.001	0.029	0.029	0.005	0.137	0.173	0.121
	FCO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	O	0.001	0.001	0.000	0.008	0.004	0.002	0.026	0.005	0.024

Table A.3. (continued)

Part 2

Scenario ID		TWL318j	TWL31Aj	TWLTHFj	TWL318c	TWL31Ac	TWLTHFc	TWL318d	TWL31Ad	TWLTHFd
Final time		30	30	30	30	30	30	1	1	1
Max T (°C)		700	700	700	1000	1000	1000	1250	1250	1250
Coolant is...		c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O
Initial Concentrations (ppm)										
Coolant		20000	20000	20000	20000	20000	20000	20000	20000	20000
O ₂		200000	200000	200000	200000	200000	200000	200000	200000	200000
Final Concentrations (ppm)										
CF ₄		4977.800	13795.000	2576.800	33018.000	42779.000	25828.000	33697.000	43503.000	27725.000
C ₂ F ₄		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₂ F ₆		7848.600	6982.200	395.170	0.000	0.000	0.000	0.000	0.000	0.000
C ₃ F ₆		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
c-C ₄ F ₈		7502.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-C ₄ F ₈		0.000	0.000	0.000	0.057	0.000	0.002	0.006	0.000	0.001
i-C ₄ F ₈ (PFIB)		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₄ F ₁₀		74.402	6628.400	0.149	0.000	0.000	0.000	0.000	0.000	0.000
c-C ₄ F ₈ O		0.000	0.000	16864.000	0.000	0.000	0.000	0.000	0.000	0.000
Solid (CF) _n		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C / O Species	CO ₂	12901.000	7404.200	2972.500	33034.000	22801.000	25842.000	34174.000	24455.000	28104.000
	COF ₂	16121.000	18328.000	6206.600	13950.000	14422.000	28330.000	11226.000	11309.000	22939.000
	CO	0.000	0.000	0.000	0.000	0.000	0.000	677.130	518.570	891.500
Oxygen	O ₂	179030	183430	195490	159990	170000	169990	159770	169540	169800
Radicals	CF ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	CF ₃	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001
	C ₂ F ₅	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	F	0.195	0.347	0.644	32.814	44.194	29.437	2533.900	3152.300	2878.700
	FCO	0.000	0.000	0.000	0.003	0.002	0.007	225.820	215.150	337.680
	O	0.037	0.013	0.086	0.000	0.000	0.000	0.000	0.000	0.000
Notes									1233°C ^a	1233°C ^a 1233°C ^a

^a Due to excessive run time, case was halted prior to completion and prior to reaching the final temperature in the profile.

Table A.4. Initial conditions and final results for MIG welding: trans-weld scenarios (anaerobic cases)

Scenario ID	TWL318f	TWL31Af	TWLTHFf	TWL318H	TWL31AH	TWLTHFH	TWL318g	TWL31Ag	TWLTHFg
Final time	30	30	30	30	30	30	30	30	5
Max T (°C)	500	500	500	700	700	700	1000	1000	1000
Coolant is...	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O
Initial Concentrations (ppm)									
Coolant	20000	20000	20000	20000	20000	20000	20000	20000	20000
O ₂	0	0	0	0	0	0	0	0	0
Final Concentrations (ppm)									
CF ₄	0.000	0.000	0.000	0.000	0.000	0.000	0.013	2.465	191.500
C ₂ F ₄	1.024	0.017	0.080	6790.000	973.330	2498.100	95.344	65.007	201.550
C ₂ F ₆	0.000	0.021	0.000	0.000	1514.200	0.254	547.680	20192.000	19824.000
C ₃ F ₆	0.000	0.000	0.000	9664.100	332.230	1272.800	23372.000	11961.000	5900.800
c-C ₄ F ₈	20000.000	0.000	0.000	9329.500	20.966	139.230	0.132	0.064	0.002
2-C ₄ F ₈	0.000	0.000	0.000	27.945	0.283	1.817	1730.400	699.750	271.660
i-C ₄ F ₈ (PFIB)	0.000	0.000	0.000	0.468	0.005	0.026	142.780	59.912	17.670
C ₄ F ₁₀	0.000	20000.000	0.000	0.001	18487.000	7.547	1.060	27.381	7.039
c-C ₄ F ₈ O	0.000	0.000	20000.000	0.000	0.000	16863.000	0.000	0.000	0.000
Solid (CF) _n	0.000	0.000	0.000	0.000	0.000	0.000	548.770	222.830	77.848
C / O Species	CO ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003
	COF ₂	0.000	0.000	0.057	0.000	0.000	3128.800	0.000	0.000
	CO	0.000	0.000	0.000	0.000	0.000	7.801	0.000	19998.000
Oxygen O ₂	0	0	0	0	0	0	0	0	0
Radicals	CF ₂	0.001	0.008	0.010	0.107	0.099	0.107	3.215	587.580
	CF ₃	0.000	0.000	0.000	0.000	0.000	0.000	0.008	95.599
	C ₂ F ₅	0.000	0.001	0.000	0.001	0.016	0.001	0.023	15.616
	F	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	FCO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
	O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Notes

974°C^a

^a Due to excessive run time, case was halted prior to completion and prior to reaching the final temperature in the profile.

Table A.5. Initial conditions and final results for MIG welding: weld-side scenarios

Scenario ID		WLD318a	WLD31Aa	WLDTHFa	WLD318b	WLD31Ab	WLDTHFb	WLD318c	WLD31Ac	WLDthfc
Final time		1	1	1	1	1	1	0.35	0.35	0.35
Max T (°C)		700	700	700	1000	1000	1000	1500	1500	1500
Coolant is...		c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O	c-C ₄ F ₈	C ₄ F ₁₀	c-C ₄ F ₈ O
Initial Concentrations (ppm)										
Coolant		10000	10000	10000	10000	10000	10000	10000	10000	10000
O ₂		100000	100000	100000	100000	100000	100000	100000	100000	100000
Final Concentrations (ppm)										
CF ₄		7.548	32.131	47.086	4493.300	6292.600	4917.400	18966.000	23930.000	18029.000
C ₂ F ₄		0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₂ F ₆		27.396	28.645	12.820	8449.300	10769.000	5578.700	0.000	0.000	0.000
C ₃ F ₆		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
c-C ₄ F ₈		9963.400	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-C ₄ F ₈		0.000	0.000	0.000	0.027	0.000	0.001	0.000	0.000	0.000
i-C ₄ F ₈ (PFIB)		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₄ F ₁₀		1.560	9960.200	0.012	0.000	0.000	0.000	0.000	0.000	0.000
c-C ₄ F ₈ O		0.000	0.000	9936.700	0.000	0.000	0.051	0.000	0.000	0.000
Solid (CF) _n		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C / O Species	CO ₂	36.535	21.148	60.246	12946.000	7064.600	10494.000	12642.000	9500.700	9219.100
	COF ₂	41.205	48.835	120.120	5661.700	5105.500	13428.000	2067.900	2141.400	3941.400
	CO	0.000	0.000	0.000	0.000	0.000	2.284	6323.700	4428.600	8809.200
Oxygen	O ₂	99943	99955	99911	84224	90382	87791	83162	87214	89405
Radicals	CF ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	CF ₃	0.004	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	C ₂ F ₅	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	F	0.067	0.447	0.656	4.927	6.616	0.000	0.000	0.000	0.000
	FCO	0.006	0.003	0.001	0.000	0.000	0.003	0.007	0.007	0.007
	O	0.020	0.011	0.085	0.006	0.030	0.000	0.000	0.000	0.000
Notes								^a	^a	^a

^a Due to excessive run time, case was halted prior to completion.

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