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Estimation of Flammability Limits of Selected Fluorocarbons with F_2 and ClF_3

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ABSTRACT

During gaseous diffusion plant operations, conditions leading to the formation of flammable gas mixtures may occasionally arise. Currently, these could consist of the evaporative coolant CFC-114 and fluorinating agents such as F_2 and ClF_3. Replacement of CFC-114 with non-ozone-depleting substitutes such as c-C_4F_8 and C_4F_{10} is planned. Consequently, in the future, these too must be considered potential "fuels" in flammable gas mixtures. Two questions of practical interest arise: (1) can a particular mixture sustain and propagate a flame if ignited, and (2) what is the maximum pressure that can be generated by the burning (and possibly exploding) gas mixture, should ignite? Experimental data on these systems are limited. To assist in answering these questions, a literature search for relevant data was conducted, and mathematical models were developed to serve as tools for predicting potential detonation pressures and estimating (based on empirical correlations between gas mixture thermodynamics and flammability for known systems) the composition limits of flammability for these systems. The models described and documented in this report are enhanced versions of similar models developed in 1992.

1. INTRODUCTION

The purpose of this report is to discuss and document techniques and tools for estimating the behavior of potentially flammable gas mixtures that are occasionally encountered in gaseous diffusion plant (GDP) operations. This work derives from preliminary modeling efforts first carried out in 1992 by Barber and Trowbridge [1]. The flammable mixtures of interest consist of oxidizing agents such as F_2 and ClF_3 reacting with fluorocarbon or chlorofluorocarbon "fuels" such as CFC-114 ($C_2F_4Cl_2$), FC-c318 (cyclo-C_4F_8, or c-C_4F_8), and FC-3110 (n-C_4F_{10}) when mixed with a variety of diluents (e.g., N_2 and UF_6). CFC-114 is presently the primary coolant in the diffusion plants and the other two materials are candidate "second generation coolants," replacements for CFC-114 that have no stratospheric ozone depletion potential.

There are two basic questions of practical interest in diffusion plant applications related to flammable gases: (1) Can a particular mixture sustain and propagate a flame if it is ignited, and (2) what is the maximum pressure that can be generated by the burning (and possibly exploding) gas mixture if it should ignite? For specific mixtures, the answers to these questions can be obtained experimentally and indeed have been for many compositions and mixtures of historical interest. Practical cases will inevitably arise that are outside the realm explicitly covered by experimental work due to variations in temperature, pressure, or composition (e.g., a mixture containing different fuels, oxidizers, or diluents or containing multiple fuels, oxidizers, or diluents). A mathematical model with a reasonably sound theoretical or pragmatic basis can assist not only in interpreting experimental results but also in interpolating, so to speak, when conditions not covered by the experimental work are encountered.

On the specific subject of flammable gas mixtures in diffusion plant applications, a considerable body of experimental work was performed on CFC-114 systems [2-4] as well as earlier coolants such as C-816, that is $C_6F_{10}(CF_3)_2$, concentrating mostly on the topic of composition limits of flammability. During the earlier GDP coolant replacement campaign, Bauer and Hamilton of 3M experimentally determined the composition limits of flammability for the $F_2/C_4F_{10}/N_2$ and $F_2/C_2F_4Cl_2/N_2$ systems [5]. Fletcher and coworkers reported work on flames of undiluted mixtures of F_2 or ClF_3 with several fluorocarbons, including c-C_4F_8 [6-8].

In 1992 E. J .Barber (now deceased) and L. D. Trowbridge each developed a prototype model relating to flame characteristics of coolant/fluorinating agent mixtures. The models were described in report K/ETO-111 [1], and brief results (minimum flammable concentrations of coolants) presented for the systems in which ClF_3 or F_2 reacted with CFC-114, C_4F_{10}, or c-C_4F_8 in diluted mixtures. At the time, the topic was considered classified, but it was being considered for declassification. The intention was to refine and more extensively calibrate and document the two models (or perhaps merge them) after declassification occurred. The subject has since been declassified, but in the interim the sponsoring program ended.

Renewed interest in coolant replacement at the GDPs has restored the motivation to complete the work begun in 1992. The original commission of this work was to document the bases and operation of the two 1992 models. After some investigation, it became obvious that it would be necessary to update and revise the models at least to a degree to allow operation with current computer operating systems and supporting software. Thus, the task expanded to include the revision of the original models. If the methods are to be usable over several years, past experience indicates that the underlying bases need to be documented so that the methods are not purely dependent on any particular software or computer architecture.

This report briefly discusses the 1992 versions of the models and the development of the 1999 versions (including theory, algorithms, and reference experimental data), presents selected results of operating the models, and finally documents operation of the current versions of the models.

2. MODEL DEVELOPMENT

2.1 EXPLOSION THEORY MODELS

2.1.1 1992 Explosion Theory Models

In 1991 and 1992, E. J. Barber developed a computer model designed to estimate the maximum pressure that could be generated on combustion or explosion of a flammable gas mixture. The fuel/oxidizer combinations consisted of pairs taken from the oxidizers F_2 and ClF_3 and the "fuels" CFC-114, c-C_4F_8 and n-C_4F_{10}. This model was also used to empirically predict the composition limits of flammability of gas mixtures such as outlined in report K/ETO-111.

Examination of Dr. Barber's archives indicates that this model actually consisted of a number of spreadsheets, each devoted to a specific narrow range of conditions: (1) the specific combination of fuel/oxidizer and, (2), within a given fuel oxidizer pair, a limited range of fuel-to-oxidizer ratios. In principle, a complete set of spreadsheets would cover all ratios of all 6 combinations of coolant/fluorinating agent. Only one fuel/oxidizer combination, however, was completely covered by the available versions and 4 other combinations were partially covered in the 22 separate spreadsheets present in the Barber computer archives.

An outline of the general method used in each of these spreadsheet versions of the model is as follows:

1. Postulate one or more characteristic reactions involved in the combustion, and assume they go to completion.
2. From the starting materials, calculate the quantities of final products.
3. Compute the energy release in the reaction.
4. Apply flame theory to predict the final pressure inside a fixed volume of gas after it burns adiabatically (i.e., without energy gain or loss).

5. Use approximations from flame and detonation theory to estimate the (brief) pressure pulse generated in a fully developed shock.

Though the results of these models were used in prediction of flammability limits, nothing in the model explicitly speaks to whether or not a gas mix would be flammable. The postcombustion temperature was used outside the context of the spreadsheet and compared with a correlation between reaction temperatures for gas mixtures known experimentally to be flammable.

Most spreadsheets postulated two bounding chemical reactions with different oxidizer/fuel ratios. For a starting gas mixture with an oxidizer/fuel ratio between that of the two reactions, the reactants are distributed between the two reactions so that complete consumption of both fuel and oxidizer occurs. Initial gas mixtures outside the bounding ratios were not valid for that particular spreadsheet. A few spreadsheets used a single reaction (those valid for very high or low reactant ratios), treating excess reactant as a diluent.

A heat of reaction is associated with each reaction in the spreadsheet. In some versions, this heat of reaction is embedded in algebraic formulae in the spreadsheet, and in others it was calculated from a table of heats of formation of each participating species. The heat of reaction for the particular mix being run, along with the change in composition upon reaction, is used as an input to a flame propagation model.

Only limited documentation of the model's physical chemistry basis was found [9]. An examination of the mathematics of the spreadsheets indicates that they are an application of a standard model of the burning of a premixed flammable gas in a spherical chamber. This constant volume spherical flame propagation model is discussed in both Jost [10] and Lewis and von Elbe [11]. The notation and format used most closely follows that of Jost [10], Chap. IV. It should be emphasized that this theory is not for detonations (supersonic shock propagation) but rather for subsonic flame front propagation. The model of an expanding spherical flame front in a fixed volume spherical chamber should, to the extent that the energetics of the reactions are representative of the actual flame process, give a reasonably accurate depiction of the final pressure attained when all the gas is burned. During burning, the flame velocity generally increases, possibly eventually running up to sonic, then to supersonic velocities, at which point this model must be discarded in favor of a direct model of fully developed detonation waves. Since the gas volumes of usual concern in GDP operations are neither spherical nor likely ignited in the center, flame velocities and local pressures may well exceed those predicted by the spherical flame propagation model. For this reason, a "detonation pressure" is estimated in the spreadsheet models, in addition to the static, pseudo-adiabatic final pressure. This detonation pressure is estimated simply as twice the final flame pressure, based on an approximation proposed by Langweiler [10]. The shock pressure is the local pressure within a moving, fully developed shock wave moving with the advancing flame front.

Nothing in the explosion theory spreadsheets directly speaks to the question of whether a given mixture will burn if ignited, though intermediate values calculated in those spreadsheets were used (outside the context of the spreadsheet calculations) to assist in such a prediction. The specific criteria used by Barber in devising the flammability boundaries reported in K/ETO-111 were not explicitly stated in that document. A search of his files did indicate the probable course of evolution of the method used. Early experimental work (1960s and 1970s) on CFC-114 systems suggested that the thermal ignition temperature for coolant plus ClF_3 or F_2 mixtures was above ~750°F (450°C) and below 1300°F (750°C) [2]. The thermal ignition temperature is that at which the mixture will autoignite, essentially a flash point for that mixture. In the late 1980s, several references in letters and memos suggested that this ignition temperature might be used as a guide to estimate flammability. The reasoning was that when a mixture burns, it should briefly reach the vicinity of its adiabatic temperature. If the calculated adiabatic temperature reached upon reaction lies below the thermal ignition temperature, insufficient energy is released to heat and ignite adjacent unburned gas.

This reasoning worked for a limited range of compositions, but when applied to a wider range of compositions, it overestimated the extent of the flammability envelope (i.e., mixtures are predicted to burn that experimentally will not do so). Closer examination of mixtures whose compositions lie on the experimental flammability boundary reveals that the predicted adiabatic temperatures vary with composition of the mixture. This became evident during the preparation of K/ETO-111, and a modified empirical method was used to predict the boundary. Based on notes from a private communication [12], the Barber flame limit estimate used in K/ETO-111 was derived as follows:

1. Select experimental points on the flammability boundary systems of interest and record the mole fractions of fuel and oxidizer on such boundary points.

2. Calculate the adiabatic temperature for these mixtures.

3. Plot the following for all these points: $T_{adiabatic}$ vs. $\ln (X_{oxidizer}/X_{fuel})$.

4. Draw or fit a straight line that lies below essentially all plotted points, deriving fit parameters A and B for the line.

5. To predict flammability limits of other (similar) systems or compositions, compute the adiabatic temperature necessary for burning at a given mole ratio. Run the (appropriately modified) model to derive the adiabatic temperature of that composition. The mixture is predicted to sustain a flame if

$$T_{adiabatic} > A \ln [X_{oxidizer}/X_{fuel}] + B \quad .$$

For calibration, compositions were taken from mixtures experimentally reported to be on the boundary of the flame envelope for F_2/CFC-114/N_2, ClF_3/CFC-114/N_2 , or F_2/C_4F_{10}/UF_6 systems. These data were taken from refs. 2, 4, and 5. The association of the flammability limit question with the 1992 explosion pressure spreadsheet models derives from the fact that the value of $T_{adiabatic}$ needed for the prediction is calculated as an intermediate value in the spreadsheet. Extracting the adiabatic temperature from the spreadsheets was a manual operation; no explicit reference to flammability prediction was present in any of the spreadsheets.

Dr. Barber's files did not contain any direct record of the specific parameters used in the preceding fit. , A few months after the publication of K/ETO-111, the present author calculated adiabatic temperatures for the same mixtures used by Barber and obtained the parameter values A = 443.5 K and B = 1273 K. These parameters were derived from thermodynamic equilibrium rather than by forcing specific reactions to go to completion. It allowed only room-temperature-stable species and (based on a memo) obtained fairly good temperature agreement with the corresponding points generated by Barber. Neither a Barber temperature list nor values for fit parameters survive. Possibly no mathematical fit was done, but rather the predictions were derived graphically.

Part of the original commission for the present work was to document the Barber model. The implicit goal, however, was to have available at the GDPs a working set of models for prediction of maximum explosion pressures that could be used for a wide variety of potential scenarios and to ensure that those models are adequately documented. With this in mind, a detailed examination of the 1992 spreadsheets was undertaken that revealed many inconsistencies from one spreadsheet version to another. A fair amount of evolution evidently took place during the preparation of the various versions, and the customization of each spreadsheet for specific limited conditions and constituents led to a variety of errors and inconsistencies. Some of these were operability errors, which did no harm to the results. Others were formula errors and led to some degree of inaccuracy in the final results. In about half the versions, a numerical convergence routine confused a Celsius with a Kelvin temperature, but this induced surprisingly little error in the answer, 5 to 15 degrees in final temperature and about 1% in pressure. In all versions, a factor relating the change in the number of moles of gas on burning was neglected, which could result in overprediction or underprediction of final pressures by tens of percent in practical cases and by multiples in pure fuel/oxidizer mixtures. A very few versions had mass balance errors. That is, the intended reactions were not properly reflected in the reactant/product conversion. Finally, there were data problems in some heat capacity information, leading to poor predictions at high temperature. Converting a particular spreadsheet for use with a different oxidizer or fuel was not at all straightforward, as many critical parameters (stoichiometry of reactions, heat of reaction, heat capacity changes) are embedded in formulae rather than present in tabular form. This difficulty of conversion almost surely led to many of the errors in some of the spreadsheets.

For these above reasons, documentation of the 1992 Barber models as they stood would be needlessly complex, would require repair and modification of all versions, and would result in incomplete coverage of the fuel/oxidizer combinations of interest. It was evident that the quickest means to the intended end would be to recreate the models in a more comprehensive form, adopting the spirit of the original design and producing a smaller number of more flexible models, along with appropriate documentation. The remainder of the discussion on spreadsheet explosion pressure models will cover these revised, more comprehensive versions.

2.1.2 1999 Explosion Theory Models

2.1.2.1 Design Intent

For the reasons just discussed, an alternate set of spreadsheets was developed following the general strategy of the Barber models, but each covering the full range of fuel/oxidizer ratios. There are six basic spreadsheets, one version for each combination of fuel and oxidizer.

The basic strategy of these new versions is similar to that of the original spreadsheet series. A set of characteristic reactions spanning a range of oxidizer/fuel ratios is postulated. Any arbitrary oxidizer/fuel ratio of interest will lie between the ratios of two characteristic reactions, or beyond the highest or lowest. Reactants are distributed between two bounding characteristic reactions so as to consume all the fuel and oxidizers. For very high or low ratios, some fuel or oxidizer will be excess and remain unreacted.

For several reasons, the new models do not calculate pressure and temperature by the original subsonic flame propagation method, as did the 1992 series:

1. The spreadsheet explosion model has been sometimes incorrectly regarded as a shock calculation (it does, however, contains an approximation to such a result).

2. Directly calculating pressure from shock theory is no more complicated than using the subsonic flame propagation theory.

3. Direct application of shock theory gives a more defensible true upper bound to pressure generation due to exploding gases.

4. The shock pressure, when estimated as twice the final subsonic explosion pressure, generally proved to be a bit higher than the shock pressure calculated by direct application of shock theory.

5. The volumes of concern are not spherical, so buildup of shock wave is more likely than in a spherical chamber.

The new set of models calculates the constant volume adiabatic (isentropic) temperature and pressure change. This calculation represents a plausible and defensible lower limit to the static pressure after a gas mixture has burned but before any heat transfer to surroundings and is straightforward to carry out. This adiabatic model also gives the Langweiler approximation to computed shock pressure. This approximation, however, should not be given as much credence as the shock pressure derived from detonation theory.

The direct application of detonation theory gives the pressure in a fully developed detonation wave (i.e. one moving at its "terminal velocity"). It also gives the shock impulse, a higher, but directional effective pressure. This impulse was neglected in the earlier model. These will be upper limits on the (very-short-duration) explosion pressure, since they calculate the terminal condition in a detonation of a particular gas mixture. In a finite volume, of course, a shock will not necessarily have the time and distance to "fully develop."

The scheme for predicting a mixture's flammability (once the empirical relationship used is calibrated) is a very simple addition and was added to the final spreadsheets.

One factor frequently considered in estimation of flame or explosion temperatures that has been ignored here is the formation of transient high-temperature species (i.e., radicals or other high temperature dissociation products of the more familiar low-temperature-stable reaction products). Estimation of the quantity of such species would require a thermodynamic treatment of the product mix at high temperature, a consideration beyond the design limits of these models. The result of inclusion of such species would be the lowering of final temperatures. Pressures would be increased due to the presence of additional (lighter) species. However, pressures would be decreased by the lower temperature, the net effect thus being unclear in the general case.

2.1.2.2 Theory

Beyond the selection of appropriate characteristic reactions and thermodynamic data, the mathematics of the new models is altered from the originals. The consequences of chemical reactions are predicted by two methods. The first calculates the adiabatic (or perhaps more properly, isentropic) pressure and temperature rise upon reaction at constant volume. The second model is a more formal detonation pressure model depicting the behavior of gas immediately behind a fully developed shock wave in a gas explosion. In either model, the chemical reactions, assumed to go to completion to the degree the available reactants permit, provide the energy to heat the gas and drive a possible detonation wave. The two models in a sense bound the subsonic flame propagation model used in the original spreadsheets, the first giving the static reaction outcome and the latter giving the worst-case effects of full detonation.

Adiabatic (isentropic) model

The adiabatic model calculates the temperature rise in product and diluent gases in a constant volume system, assuming no energy gain or loss from the system: that is, the heat of reaction will all go into heating the gases present, with none lost as heat or work to the surroundings. This is a static model, unlike the original 1992 version, which was a dynamic model of (subsonic) flame propagation.

From the ratio of fuel (coolant) to oxidizer (fluorinating agent) the model will deduce which reactions will occur and calculate final products and energy release from tables of enthalpy of formation (ΔH_f). Since this is a constant volume process, we need to determine the reaction's internal energy change, ΔE, rather than its enthalpy change, ΔH. The two are related per:

$$\Delta E = \Delta H - \Delta(PV) \quad .$$

Since ΔE is a state function, it does not depend on the route chosen from initial to final conditions, but only on the physical parameters at the end points. We imagine first that the reaction takes place (at constant volume and temperature), with a possible change in the number of moles of gas. Treating all gases as ideal,

$$\Delta(PV) = \Delta n\, RT \quad .$$

Consequently, the internal energy change for this segment is

$$\Delta E(T_i) = \Delta H(T_0) - \Delta n\, RT_0 \quad .$$

Here, ΔE, ΔH, and T are evaluated at the standard thermodynamic reference temperature, T_0, of 298.15K, and at standard pressure. The term Δn is obtained from the reaction stoichiometry (representing the gain or loss in numbers of moles of gas). At standard temperature and pressure, ΔH is obtained from appropriately weighted sums of tabulated enthalpy of formation data for reactants and products. To correct ΔE from the tabulated value at the reference temperature to the initial temperature T_i, the following adjustment must be applied:

$$\Delta E(T_i) - \Delta E^\circ = \int_{T_0}^{T_i} C_V dT \quad .$$

Since for an ideal gas, $(dE/dV)_T$ is zero (i.e., the internal energy is independent of volume at constant temperature), no correction is needed if the initial pressure is other than the standard thermodynamic reference pressure of 1 bar. The term ΔE represents the energy released at constant volume upon completion of the reactions postulated. The second part of the problem is to calculate the temperature to which the product mixture will rise as it absorbs this energy. The temperature change is obtained by solving the integral equation

$$-\Delta E = \int_{T_i}^{T_f} C_V dT \quad .$$

The minus sign is present because we are returning the heat of reaction to the system Tabulated in the spreadsheets are coefficients for polynomial fits for C_P, the constant pressure heat capacity, in the following form:

$$C_P = a + b/T + c/T^2 + d/T^3 + e/T^4 \quad .$$

We need the constant volume heat capacity, which, for ideal gases, is

$$C_V = C_P - R \quad .$$

Thus the polynomial form of C_V is

$$C_V = a - R + b/T + c/T^2 + d/T^3 + e/T^4 \quad ,$$

and the temperature-integral form of this is

$$\int_{T_i}^{T_f} C_V dT = (a - R)\,T + b \ln T - c/T - d/2T^2 - e/3T^3 \Big|_{T_i}^{T_f}$$

To determine the temperature rise in the product mixture, which may consist of reaction products, unreacted reactants, and diluents, we need the average heat capacity of the mixture. Since the functional forms used in the spreadsheet models for C_P and C_V are identical for all participating species (except for the values of coefficients a, b, c, d, and e) we can conveniently determine the heat capacity for mixtures by adding the corresponding coefficients, appropriately weighted:

$$C_{V,mixture} = \sum_s X_s \sum_{k=0}^{4} f_{k,s} T^{-k}$$

where s is the identifier for each species present, X is a mole fraction, and $f_{k,s}$ is the C_V coefficient for the polynomial fit for species s. Solving for T_f is done by a numeric convergence method. Rearranging the heat capacity integral yields the following form:

$$(a - R)\,\Delta T = \Delta E - b\,\Delta \ln T + c\,\Delta \frac{1}{T} + d\,\Delta \frac{1}{2T^2} + e\,\Delta \frac{1}{3T^3} \quad .$$

Here, an uppercase delta (Δ) preceding a temperature functions indicates the difference between the initial and final values of that function. For example, "$\Delta \ln T$" means "$\ln T_f - \ln T_i$." The numerical method used begin with an estimated value (that is, a guess) for T_f. That value is then used to compute the values on the right hand side of the equation and then to solve for ΔT (and hence T_f) on the left hand side. The new value for T_f is used for the next guess and the process is repeated until the guess and the solution converge to a common value. Once T_f is found, P_f will be determined by the ideal gas law. The resulting final values are presented in the models as the "final" results under the heading of "adiabatic case."

As in the original spreadsheet series, a "detonation pressure" is estimated as simply twice the calculated adiabatic pressure per the Langweiler approximation (see ref. 3, p. 172). Langweiler also approximated the detonation temperature as:

$$T_2 = 2\,\gamma\,/\,(\gamma + 1)\,T_f$$

where T_f is the adiabatic temperature attained by combustion and γ is the heat capacity ratio c_P/c_V. It is not clear at what temperature γ is to be calculated, but the result will not vary a great deal with this choice. The spreadsheet models calculate γ for this purpose at T_f. The temperature immediately behind the shock front, T_2 is also listed in the "adiabatic model" under "detonation."

Detonation model

Throughout this and the previous section, several distinct physical environments should be defined. The initial condition is user specified, and is generally near room temperature and atmospheric pressure. It is designated by the subscript "i" in the adiabatic calculations and "1" (following both the Lewis and von Elbe [11] and Jost [10] notation) in the detonation model. The adiabatic endpoint, designated here by the subscript "f" (final), is the endpoint reached if the gas simply reacts to the specified final products and is heated by its heat of reaction. The "detonation" or "shock" condition is that which applies immediately behind a fully developed shock wave. It may take some time and distance for an initiated flame to accelerate to a shock, especially when the reactant mix is barely within the region of compositions permitting explosions. The shock conditions will persist locally only briefly, being dissipated behind the shock at what must be about the local speed of sound. The shock condition represents both a moving compression wave and physical movement of the gas at the shock front, pushed by the flame and explosion immediately behind the front. This leads to a final pressure-like term called the impulse, which is the momentary force per unit area exerted by the combination of the post-shock pressure plus the momentum of the moving gas. This impulse will persist for the duration of the passage (or arrival) of the shock front, which will be moving at supersonic speed (relative to sound speed in the unburned gas). The momentum portion of the impulse is directional, exerting force in the direction of the bulk motion of gas in the shock but not perpendicular to that motion.

Texts by Jost [10] and by Lewis and von Elbe [11] discuss detonation waves in burning gas mixtures in similar same terms. The notation used here follows that of Lewis and von Elbe [11], and the equation numbers are those found in that reference (Chap. VIII, p. 524ff). The theory of gas detonations is based on Hugoniot curves, which relate preburn and postburn pressures and specific volumes under shock and nonshock conditions. Key points of this detonation model are repeated here. Two equations

$$\frac{v_1^2}{v_2^2} - \left(1+\frac{1}{\gamma_2}\right)\frac{v_1}{v_2} + \frac{n_1 T_1}{n_2 T_2 \gamma_2} = 0 \qquad (21)$$

and

$$\langle C_V \rangle \left(T_2 - T_1\right) - \Delta E - \frac{R}{2}\left(\frac{v_1}{v_2} - 1\right)\left(n_2 T_2 + n_1 T_1 \frac{v_2}{v_1}\right) = 0 \quad , \qquad (22)$$

must be solved for the two unknowns v_2 and T_2. The definitions of some of these variables are not what one might first imagine. The variable v is the volume of a unit mass of gas at condition 1 or 2, the pre-shock and shock condition, respectively, while n is the number of moles per unit mass of the gas at condition 1 or 2. Therefore ΔE and $\langle C_V \rangle (T_2 - T_1)$ must be in units of energy per gram of product gas. The factor $\langle C_V \rangle$, intended to mean the average C_V between T_1 and T_2 of the product gas mix, is variously taken as the linear average of $C_V(T_1)$ and $C_V(T_2)$, as the integral of $C_V\,dT$ from T_1 to T_2 divided by $(T_2 - T_1)$, or sometimes (for ease of calculation) simply as $C_V(T_2)$. The integral form, the most accurate and defensible, is used in these models.

These equations are solved iteratively by a convergence technique. Using an initial guess for T_2, Eq. (21) is solved for the ratio v_1/v_2. It may have two branches, one corresponding to a supersonic shock, and the other to a slow flame. The solution of interest here is the higher value. Inserting this value for v_1/v_2 in Eq. (22), we solve for T_2. This becomes our next guess. New values for temperature-dependent parameters are computed from the new T_2 (i.e., $\langle C_V \rangle$ and γ_2) and we iterate through Eqs. (21) and (22) until the value of T_2 converges.

Once v_2 and T_2 have been determined, other parameters are derived. The parameter P_2 is obtained from the ideal gas law, which for the variable definitions used here, is

$$P_2\, v_2/n_2\, R\, T_2 = P_1\, v_1/n_1\, R\, T_1 \quad . \qquad (23)$$

The detonation velocity, D is obtained from

$$D = \frac{v_1}{v_2}\sqrt{\gamma_2 n_2 R T_2} \quad . \qquad (24)$$

The shock impulse is given by

$$i = (P_2 - P_1) v_1/v_2 \quad , \qquad (11)$$

which has units of pressure and includes both the local shock pressure and the momentum term due to local movement of gas.

The pressures and temperatures calculated from this model are presented in the summary section of the spreadsheets under the heading "Detonation Model." The "Shock" entries give the T and P values (in various units) within the shock wave. The "Impulse" pressure includes both the shock pressure and the (directed) equivalent pressure due to gas movement.

2.1.2.3 Flame Limits

The 1992 prediction of flammability was based on a correlation between composition and adiabatic temperature. The reconstituted (1999) detonation theory spreadsheets do not contain the identical calculation of adiabatic temperature as the original models (a constant volume, isentropic, temperature is calculated rather than the constant pressure adiabatic temperature as in the original); the final temperature is calculated in an analytically more accurate manner; thermodynamic parameters are in some cases different). Because of these differences, a revised calibration is needed. Keeping the spirit (and functional form) of the original technique, but using the isentropic temperatures calculated in the new model series, an equation bounding experimental data at flammability boundaries for several fuel-oxidizer systems similar or identical to those of interest yields the following formula: "a mixture is predicted to be flammable if its isentropic temperature after reaction exceeds the larger of 800K or [250K ln ($X_{oxidizzer}/X_{fuel}$) + 1251K]. Details of the calibration of this equation are contained in Appendix D.

2.1.2.4 Model Implementation

The 1999 version of the explosion theory model is implemented in spreadsheet form. The model was developed in Quattro Pro 8 format (part of Corel's WordPerfect Office Suite 8), but was also converted to Lotus 1-2-3 (version 5) and Microsoft Excel 97. Six versions of the model were developed, one for each combination of two oxidizers (F_2 or ClF_3) with three fuels (coolants CFC-114, c-C_4F_8, or C_4F_{10}). Each spreadsheet is suitable only for reactions involving its specific pair of reactants. Normal user inputs are initial temperature, pressure, volume, and starting gas composition. Results are calculated automatically when input values change. Key output values are collected in a summary table, consisting of temperatures and pressures at several conditions (e.g., at the final adiabatic condition and at shock conditions). Details of operation of the models are contained in Appendix A.

Algorithms

The fundamental chemical assumption in the model is that the reaction of fuel and oxidizer can be approximated by specified chemical reactions that are assumed to go to completion to the extent permitted by the available quantities of reactants. For each fuel/oxidizer combination, a series of chemical reactions is specified, each requiring varying ratios of fuel and oxidizer. The specific reaction lists used are contained in Table 1.

Table 1. Characteristic reactions for detonation pressure (spreadsheet) models

System	Oxidizer/fuel ratio	Characteristic reactions
$F_2 + \text{CFC-114}$	1:1	$C_2F_4Cl_2 + F_2 \rightarrow 2\ CF_3Cl$
	3:1	$C_2F_4Cl_2 + 3\ F_2 \rightarrow 2\ CF_4 + 2\ ClF$
$F_2 + c\text{-}C_4F_8$	1:1	$F_2 + C_4F_8 \rightarrow C_4F_{10}$
	2:1	$2\ F_2 + C_4F_8 \rightarrow 2\ C_2F_6$
	4:1	$4\ F_2 + C_4F_8 \rightarrow 4\ CF_4$
$F_2 + C_4F_{10}$	1:1	$F_2 + C_4F_{10} \rightarrow 2\ C_2F_6$
	3:1	$3\ F_2 + C_4F_{10} \rightarrow 4\ CF_4$
$ClF_3 + \text{CFC-114}$	1:3	$ClF_3 + 3\ C_2F_4Cl_2 \rightarrow C_2F5Cl + 2\ CF_3Cl + 2\ CF_2Cl_2$
	1:2	$ClF_3 + 2\ C_2F_4Cl_2 \rightarrow 3\ CF_3Cl + CF_2Cl_2$
	1:1	$ClF_3 + C_2F_4Cl_2 \rightarrow CF_3Cl + CF_4 + Cl_2$
	4:3	$4\ ClF_3 + 3\ C_2F_4Cl_2 \rightarrow 6\ CF_4 + 5\ Cl_2$
	3:1	$3\ ClF_3 + C_2F_4Cl_2 \rightarrow 2\ CF_4 + 5\ ClF$
$ClF_3 + c\text{-}C_4F_8$	1:1	$ClF_3 + c\text{-}C_4F_8 \rightarrow ClF + C_4F_{10}$
	2:1	$2\ ClF_3 + c\text{-}C_4F_8 \rightarrow 2\ CF_4 + 2\ CF_3Cl$
	4:1	$4\ ClF_3 + c\text{-}C_4F_8 \rightarrow 4\ CF_4 + 4\ ClF$
$ClF_3 + C_4F_{10}$	1:1	$ClF_3 + C_4F_{10} \rightarrow ClF + 2\ C_2F_6$
	3:1	$3\ ClF_3 + C_4F_{10} \rightarrow 3\ ClF + 4\ CF_4$

Any arbitrary oxidizer/fuel ratio of interest will lie between the ratios of two characteristic reactions, or beyond the highest or lowest. Reactants are distributed between the next higher and lower stoichiometric ratios so as to consume all the fuel and oxidizer as both reactions go to completion. For very high or low initial ratios, some fuel or oxidizer will be excess and remain unreacted. The final composition is calculated by adjusting the initial composition for gain of reaction products and loss of reactants.

Reactive species other than the specified fuel and oxidizer do not participate. This reaction formulation does not reasonably permit calculations on mixed fuels or oxidizers, since it requires the user to specify which reactions go to completion (depending on the oxidizer/fuel ratio), with no provision for choosing or distributing mixed reactants.

The energetics of the reactions provide the energy to heat the reaction products and diluent gases. This will determine the temperature and pressure rise in a constant volume system according to two different models (as discussed in detail in Sect. 2.1.2.2). Realistic results, then, depend to a significant degree on whether the chosen reactions are those that actually occur, or at least are energetically representative of such reactions. The heat of reaction for the system as a whole is calculated indirectly by simply multiplying the enthalpy of formation of each species by the number of moles of that species for both initial and final mixtures and then summing appropriately.

The overall heat of reaction, the initial and final composition, and the initial temperature, pressure, and volume provide the inputs needed to compute the final temperature and pressure according to the two models discussed in Sect. 2.1.2.2 (the "adiabatic temperature" model and the "detonation theory" model). The algorithms used for calculating the final pressures straightforwardly follow the descriptions given in the theory section. Heat capacity as a function of temperature is required by both models. The heat capacity for the final mixture is calculated as a mole-fraction weighted sum of heat capacities of each of the constituents.

Data

The models require specific reaction and thermodynamic data. These include a reaction list for each chemical system and thermodynamic data for each reactant, product, or diluent that may be of interest.

Systems and reactions. To the extent possible, the same set of characteristic reactions is used as in the corresponding 1992 set of models, though there were sometimes inconsistencies in a series of reactions (i.e. different reactions in two spreadsheets with the same fuel/oxidizer ratio) that had to be resolved in the new models. The reactions used are listed in Table 1.

A variety of compounds are included in the list of species that can be incorporated into a calculation. These include, of course, the reactants and products listed in Table 1, but also additional species that may be included as inert diluents (e.g., N_2, O_2, HF, HCl, ClO_2F, ClO_3F, UF_6, and SiF_4).

Thermodynamic data. Thermodynamic properties used in the original spreadsheet series varied somewhat from one version to another. In the present versions, ΔH_f° values are taken from the JANAF Thermochemical Tables [13] and NBS sources [14] where available.

Formulae for C_P from the original spreadsheet series, where available, were retained in their original inverse power series format. For perfluorocarbon-related species (c-C_4F_8, C_4F_{10}, and products thereof), such formulae were not present in the original spreadsheets, and the C_P formulae for CFC-114 and CFC-115 exhibited unphysical behavior at high temperatures. For these compounds, estimates were made, with the formulae pegged to the limited number of known low temperature data points, and forced to approach a high temperature limiting value plausible on statistical mechanical grounds, that is,

$$C_P \approx (3n - 3) R ,$$

when the temperature is high enough to saturate vibrational modes, n being the number of atoms in the molecule). For all species C_P formulae were checked for reasonable behavior from 300 to 4000 K and several were refit to improve agreement with published tabular data from ref.13. Values used in the model for the thermodynamic parameters needed are listed in Appendix C, Table C.1.

2.2 EQUILIBRIUM-BASED FLAME LIMIT MODEL

2.2.1 1992 Equilibrium-Based Flame Limit Model

In ref. 1, the second model used to predict flame limits for fluorocarbon/fluorinating agent gas mixtures was based on an empirical correlation observed between the adiabatic thermodynamic temperature of gas mixtures and the flammability of those mixtures. The adiabatic temperature is that attained by the mixture when it reaches thermodynamic equilibrium at constant pressure without gain or loss of thermal energy outside the system (though, at constant P, expansion does transfer work to the outside). A typical chemical system allowed gaseous components including reactants, inert diluents, and potential reaction products. For flammable gas mixtures, the equilibrium condition will strongly favor the formation of reaction products (e.g., CF_4) at the expense of reactants (e.g. F_2 and c-C_4F_8). The user needs only to consider possible products, however, and is not required to designate exactly which will form or in what proportions. The calculation of the equilibrium state (done with the aid of thermodynamics software) will determine the product mix.

Prediction of flame limits was based on purely empirical correlations observed between the adiabatic temperature of "reacted" gas mixtures known experimentally to lie on the composition limits of flammability and some simple functions of mixture composition.

Several correlations were examined, and none were perfectly satisfactory at matching all available experimental boundary data points. The correlation finally used was one that bounded known flammability composition boundary points for the specific systems of interest (or for closely related systems). Specifically, two boundaries were established: one for rich mixtures,

$$T_{rich} = A_{rich} / X_{fuel} + B_{rich} ,$$

and the other for lean mixtures

$$T_{lean} = A_{lean} / X_{oxidizer} + B_{lean} \quad .$$

"Rich" mixtures were defined as those having an excess of fuel and "lean" mixtures as having an excess of oxidizer relative to the ideal stoichiometric fuel/oxidizer ratio which would burn the fuel to CF_4. The parameters A and B were calibrated using available experimental data so that the adiabatic temperature computed for any lean mixture on or within a flammability boundary would equal or exceed the value of T_{lean} (and similarly for rich mixtures). To allow the predicted temperature to make a smooth transition between lean and rich mixtures, a smoothing function was used:

$$T_{threshold} \quad = \quad (T_{lean}{}^{N} + T_{rich}{}^{N})^{1/N}$$

where a reasonable smoothing was achieved using a value for N of minus 4. Values of parameters used in in the 1992 model were as follows: $A_{lean} = 71$, $B_{lean} = 1036$, $A_{rich} = 55$, and $B_{rich} = 758$.

The model as previously described, was essentially conceptual, tied to no particular software. It was tied to data in that the experimental flame boundary data points used in the calibration defined which mixtures are deemed to burn and also was tied to thermodynamics data (and choice of product species), which determined the calculated adiabatic temperatures associated those mixtures. In practice, since many calculations had to be performed either for generating the adiabatic temperatures used in calibration or for computing points on the composition limits of flammability, automated systems were developed. All were based around SOLGASMIX, a computational thermodynamics program of long genealogy. The version used in 1992 predates the one described in refs. 15 and 16, and is incompatible with current data libraries and utilities for that program.

2.2.2 1999 Version of Equilibrium-Based Flame Limit Model

One part of the original commission of this present work was to adequately document the 1992 model so that it could be routinely applied to current GDP problems relating to gas flammability. Examination of the 1992 model revealed that to provide a usable version, some revision would be necessary to render it compatible with current operating systems (e.g. Microsoft Windows 95 or 98) and the most recent documented version of SOLGAS [16].

2.2.2.1 Design Intent

At its simplest, this model is a prescription for estimating the flammability of a potentially combustible gas mixture based on the observed behavior of similar chemical systems. It requires thermodynamic data for a reasonable set of reactants and reaction products and a means (generally via a computer program) for calculating the thermodynamic equilibrium and temperature at adiabatic conditions. Two basic operations are needed in the development and use of the conceptual model: (1) calculation of adiabatic temperatures of mixtures experimentally observed to burn (or not burn) and (2) determination of the predicted composition limits of flammability for a gas mixture.

Calculation of the adiabatic temperature of a gas mixture on burning is a fairly straightforward thermodynamics problem. The adiabatic temperature might be needed for gas compositions experimentally known to burn or not burn (to be used for calibration of the model, or to compare with the predicted threshold temperature for flammability, discussed in the next section). Finding a boundary point on a composition envelope is a matter of computing the adiabatic temperature of that composition and also the predicted threshold temperature, then adjusting the composition in such a way as to find a composition at which the two are equal. Software has been developed to automate much of this process (to be discussed later in more detail).

2.2.2.2 Theory

There is no particular basis in theory from which to simply predict the ignitability or lack thereof for a gas mixture. Ignition of a flammable gas mixture is a complicated balance between heat generation (by combustion), heat dissipation (convection, conduction, radiation, absorbtion by diluents), and reagent depletion. Nevertheless, the concept of "ignition temperature" (a temperature that, if reached by the combusting gas, implies that a flame in the gas can propagate) has been used in other systems. For example, for hydrocarbon/oxygen flames, adiabatic combustion temperatures on the order of 1300 – 1350°C generally imply a combustible mixture (ref. 11, p. 319). The original concept in diffusion plant-sponsored flammability boundary work held that the appropriate "ignition temperature" for fluorine/CFC-114 mixtures was between 750°F (450°C) and 1300°F (750°C) [2], and originally a constant value of the adiabatic temperature was proposed as a boundary between flammable and nonflammable mixtures. When examined in detail over a wide range of compositions, and when applied to other chemically similar systems, this constant value significantly overpredicted flammability boundaries. Trends appear in plots of adiabatic temperature vs various arbitrary functions of composition. A number were examined in the 1992 campaign, and re-examined during the present work. The one that proved the most reliable predictor of flammability boundary (though by no means perfect for all systems) was a slightly modified version of the 1992 function. Again, two boundaries were established: one for rich mixtures,

$$T_{rich} = A_{rich} / (S\ X_{fuel}) + B_{rich} \quad ,$$

and the other for lean mixtures:

$$T_{lean} = A_{lean} / X_{oxidizer} + B_{lean} \quad ,$$

with the two being smoothly combined to give a single threshold temperature:

$$T_{\text{threshold}} = (T_{\text{lean}}^{N} + T_{\text{rich}}^{N})^{1/N}$$

where $N = -4$. The function for T_{rich} is slightly altered from the 1992 version by the addition of a divisor "S," which is a stoichiometry factor indicating the number of moles of oxidizer required to completely react the particular fuel to CF_4 (and, if Cl-containing compounds are present, to Cl_2). Addition of this factor improved the correlation somewhat for systems whose fuels differed greatly in per-molecule demand for fluorine. An operational result of this addition, however, is that while one can readily determine a value for S for any single fuel/single oxidizer system, the corresponding value for gases containing multiple fuels or oxidizers will depend on the specific proportions of each. In its present form, then, it is somewhat inconvenient to run cases with multiple fuels or oxidizers. In any case, there are no experimental data with which to compare results of multiple fuel/oxidizer.

Recalibration used the present set of thermodynamic data. Correlations for both lean and rich threshold formulae were established yielding conservative values for the fit parameters: $A_{\text{lean}} = 70$, $B_{\text{lean}} = 1050$, $A_{\text{rich}} = 95$, and $B_{\text{rich}} = 800$.

These are conservative in the sense that they produce a boundary that has been adjusted to allow a margin of error between the correlation function and the nearest experimental data points to allow for system-to-system variation in data and sparseness of calibration data in some composition regimes. Details of the calibration are discussed in Appendix D.

2.2.2.3 Implementation in Software

The complex part of this model is the calculation of thermodynamic equilibria and adiabatic temperatures. In principle, any thermodynamics program could be used for this system as long as the program is capable of computing chemical equilibria for gaseous mixtures and providing either adiabatic temperature information or heat gain or loss. We use the 1995 version of SOLGAS described in ref. 16 for reasons of familiarity, convenience, and (not least) the fact that it is documented (whereas the 1992 version was not). SOLGAS computes thermodynamic equilibria for gas mixtures and provides information on heat evolution as part of its output, but does not directly determine the adiabatic temperature (that is, the temperature at which the heat of reaction is exactly balanced by the heat absorbed by the product mix). To perform that operation, a utility called ADIABAT was developed that repeatedly runs SOLGAS, altering the final temperature of the product mix until it converges to the adiabatic value. The version of SOLGAS as described in ref. 16 is used without modification in the current system. ADIABAT, also described in ref. 16, had to be modified slightly for operation under Windows 95, ADIAB95.EXE being the modified version. ADIAB95 simply finds adiabatic temperatures for one or more specified gas mixtures and creates output in spreadsheet-importable format. ADIAB95 does not calculate the threshold temperature, though this can be done via a single formula referencing the results file after import into a spreadsheet.

A second utility for SOLGAS was developed in 1992, this one designed to repeatedly run SOLGAS, altering one reactant's initial quantity (thereby altering the overall composition) until it found a composition whose adiabatic temperature matched the empirical threshold temperature for predicted flammability. That program, too, had to be altered for use with Windows 95, the resulting 1999 version being named FLAME4d.EXE. Its output is also in spreadsheet-importable format, and consists of a series of compositions predicted to lie on the flammability boundary.

Both the SOLGAS utilities are designed to take a list of initial conditions (pressure, composition, and temperature) and operate on each member of the list without user intervention (beyond the initial specification of the list and chemical system). Details of operation are described in Appendix B.

Data

Calibration and operation of this model rely on several sources of data. These include (1) the chemical systems considered as reactants, (2) the species considered as potential reaction products, (3) thermodynamic data for such species, and (4) experimental data for specific compositions known to be ignitable or not ignitable.

Chemical systems. The model is calibrated against flammability boundary data for a number of similar fuels and oxidizers. The full list of systems is discussed in Appendix D. Oxidizers are limited to F_2 and ClF_3, and the fuels, to light perfluorocarbons (C_2F_6, C_3F_8, c-C_4F_8, and CFC-114, that is, $C_2F_4Cl_2$). Calibration data are either for binary systems (fuel plus oxidizer only) or for ternary systems in which the diluent is N_2.

We will later calculate and present results for the three coolants of primary interest (c-C_4F_8, C_4F_{10} and CFC-114) reacting with F_2 or ClF_3 diluted by either N_2 or UF_6. In the calculations, UF_6 is treated simply as a diluent. No provision is made for UF_6 participating as an oxidizer. The rationale is that relatively little heat of reaction would be generated by UF_6 relative to its heat capacity: about 68 kcal/mol energy is required to generate F from UF_6 dissociation compared with about 19 kcal/mol for F produced by dissociation of F_2.

Species list. The thermodynamic equilibrium calculation requires specification of a list of potential reaction products. In addition to the starting species (fuel, oxidizer, and diluent), possible reaction products are included, both stable species and radicals. The full list of species considered in the calculations performed for this report is itemized in Appendix C, Table C-2.

The list of possible reaction products excludes elemental carbon. All the higher fluorocarbons and chlorofluorocarbons are thermodynamically unstable relative to decomposition to CF_4 and graphite, and the energetics of such disproportination reactions are such as to lead to the prediction that most could react or explode in the absence of any oxidizer whatever. Empirically, however, no rapid conversion to CF_4 and elemental carbon is observed. Even at high temperatures, decomposition proceeds to CF_2 and CF_3 with only a very slow buildup of species of lower and higher fluorine content. Since we are interested in reactions that occur rapidly (omn the time scale of the passage of a detonation wave), only those species are included which experimentally are observed to be form in significant quantity under such conditions. Elemental carbon (i.e. graphite) is not among such species, so graphite is simply not included in the list of possible products.

Thermodynamic data. Thermodynamic data for the species considered are derived largely from the JANAF Thermochemical Tables when available. Tabular data for C_P were fit to the polynomial temperature function used by SOLGAS. The fit covers the temperature range from 300 K to at least 4000 K. Specific values used for each species are listed in Appendix C, Table C.2.

Flame limit calibration data. Data points known to be on or near flammability limits were used for calibration of the empirical functions in the model. The data used are the same ones used for calibrating the flammability limit prediction in the detonation pressure model. Calibration details are discussed in Appendix D.

3. RESULTS AND DISCUSSION

3.1 DETONATION PRESSURES

The theory of detonations in combustible gas mixtures is well developed and well established. However, no known available experimental data give shock pressures or temperatures for fluorocarbon/fluorine systems with which to compare the results of these models. A variation of the model was developed using an 8:1 hydrogen:oxygen mixture in order to compare results with an example presented in ref. 11. When radical products were included in the modified spreadsheet version, the shock temperature, pressure, and velocity computed by this model agreed within 1.8% with the tabulated theoretical results and within 6% with the experimental shock velocity. The small differences are likely due to differences in thermodynamic values used or computational approximations made.

The detonation pressure models were developed as tools to apply to specific conditions as the needs arise. No single narrow set of conditions are of special interest as this is being written, however. Appendix A, which describes the operation of the spreadsheet versions of these models, does so partly by detailed illustration of a sample problem.

Some general observations on the relative reactive potency of the coolants and oxidizers under consideration can be made from results of these models. As a reference condition, consider the case of a gas at 25°C and 1 atm total pressure in which 60 mol % of a gas mixture consists of diluent, the diluent consisting of UF_6 at its vapor pressure (14.7%) and N_2 comprising the balance of the diluent (45.3%). The remaining 40% of the gas will be a fuel/oxidizer mix, with the ratio being chosen as that which gives the highest detonation pressure. For the six combinations of fuel and oxidizer, the results are shown in Table 2.

Table 2. Pressure results for the most potent fuel/oxidizer mixtures. The gas mixture consists of a diluent comprising 14.7% UF_6 and 45.3% N_2, with the remaining 40% being the fuel/oxidizer mixture at the listed ratio.

Oxidizer	Fuel	Ratio of oxid:fuel	Isentropic (const. vol.) pressure, (atm)	Detonation pressure, (atm)	Impulse, (atm)
F_2	CFC-114	3:1	7.4	14.4	24.3
F_2	c-C_4F_8	4:1	9.8	19.1	33.5
F_2	C_4F_{10}	3:1	8.7	17.0	29.5
ClF_3	CFC-114	4:3	8.8	17.1	29.5
ClF_3	c-C_4F_8	2:1	10.4	20.3	35.9
ClF_3	C_4F_{10}	3:1	8.6	16.7	28.8

The pressures listed in the table are the isentropic value (i.e., the final constant volume adiabatic pressure that the heat of reaction can generate prior to any heat loss to the surroundings); the detonation pressure, (i.e., the transient pressure within a fully developed shock wave); the impulse, (a combination of the detonation pressure and the momentum of the gas in the direction of motion of the shock wave). To reiterate earlier comments, the fact that the model computes a detonation pressure and impulse is no guarantee that a fully developed shock will arise; these values simply represent the upper limit of transient pressures that could possibly be generated.

Viewed in this way, it can be seen that the two perfluorocarbons can generate higher pressures than CFC-114, and that ClF_3 has the potential to generate slightly higher pressures than F_2. The order of "potency" however, could change if the rules of comparison changed – for example, a series of 1:1 oxidizer:fuel ratio mixtures would yield higher pressures for CFC-114 explosions than for the perfluorocarbon.

3.2 FLAMMABILITY LIMITS

The detonation pressure models also evaluate the predicted adiabatic temperature of the gas mixture against the threshold temperature and predict whether or not the gas mixture is ignitable. One can generate a list of points predicted to lie on the boundary by seeking compositions for which the two temperatures are identical, a process that can be very laborious if done manually. The process can be automated somewhat but such automation is not incorporated into the six detonation model spreadsheets.

In Appendix D, two set of calibration parameters were developed for each flame limit model, one termed the "best fit" and the other a "conservative fit." The former represents the correlations that most tightly bound the available experimental flammability limit data, while the latter relaxes the correlation function somewhat to anticipate system-to-system variations in the correlation function. The boundaries plotted in Fig. 1 through 16 derive from the "conservative fit" correlations. Each figure displays the equilibrium-based model's prediction of the composition boundary of flammability. These were done for gas mixtures starting at 1 atm and 25°C, though the boundaries shift little for moderate changes in initial temperature or pressure. For the systems covered by the detonation theory models, that prediction is also plotted. Despite the nomenclature, the prediction is not really related to detonation theory, per se, but rather to the predicted constant volume adiabatic temperature calculated for the specific reactions used in those models. Publicly available ternary (i.e., oxidizer/fuel/diluent) flammability data on these systems are sparse; binary data (i.e., oxidizer/fuel mixtures) are more prevalent. Available data for these systems are plotted in the appropriate figure. Most of the experimental data consist of compositions at or very near a flammability boundary. Some plotted data are points that lie well within the region of flammability and a few points are shown that were found to be non-ignitable.

Examination of the boundaries and data points shown in these figures should give an impression of the degree of conservatism inherent in the models' predictions. For CFC-114 and c-C_4F_8, the model predictions are a few percent in composition more conservative in their prediction of flammability than available data points indicate. A few percent, however, can represent a significant difference when the minimum flammable concentration itself is only a few percent, as can be seen in Figure 3, which indicates an experimental minimum flammable concentration of c-C_4F_8 of about 7%, versus a predicted value of about 3%.

Lack of smoothness in flammability envelopes for the detonation model predictions (as can be seen in Figures 2, 6, and especially 10) is an artifact of changes in oxidizer/fuel ratio, which causes the model to make a transition from one set of reactions to another.

Potential system-to-system variation is illustrated by the more severe over prediction of flammability limits apparent in the C_3F_8 and C_2F_6 systems (Figures 13 through 16). For both coolants, the F_2 predictions overestimate the flammability limits by about 10% for lean mixtures (no experimental boundary points were found for rich mixtures in those two systems). The corresponding ClF_3 systems overestimate the flammability boundaries by about 20%.

Table 3 lists the minimum flammable concentrations for each of the 12 combinations of fuel (CFC-114, c-C_4F_8, or C_4F_{10}), oxidizer (F_2 or ClF_3), and diluent (N_2 or UF_6). These compositions for the two models are chosen from the flammability boundaries displayed in Figs. 1-12, and represent the minimum concentration of either oxidizer or fuel which is flammable. Where

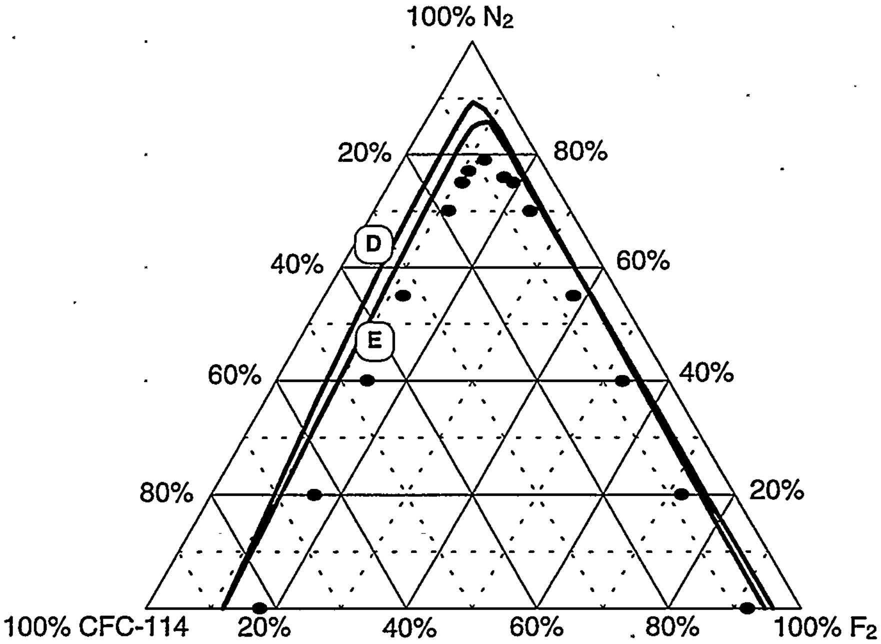


Fig. 1. Flammability boundaries for F_2/CFC-114/N_2 mixtures.
D = detonation theory prediction; E = equilibrium-based prediction;
solid circle = data point on flammability boundary.

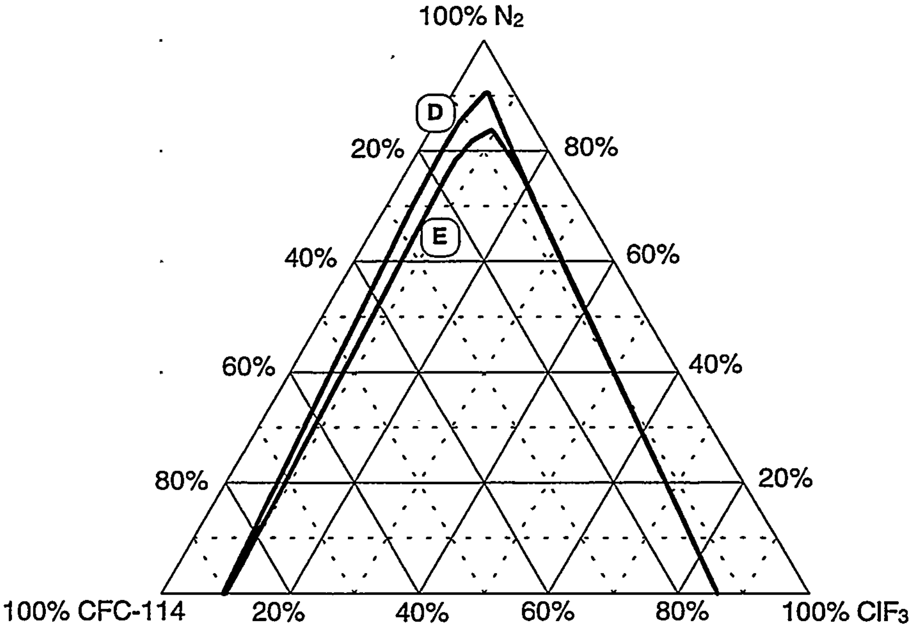


Fig. 2. Flammability boundaries for ClF_3/CFC-114/N_2 mixtures.
D = detonation theory prediction; E = equilibrium-based prediction.

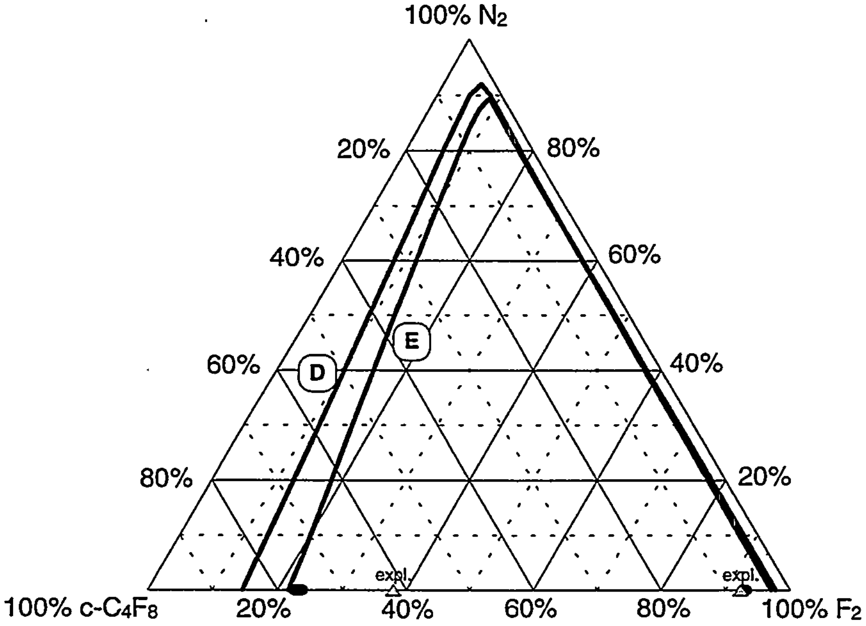


Fig. 3. Flammability boundaries for F_2/c-C_4F_8/N_2 mixtures. D = detonation theory prediction; E = equilibrium-based prediction; solid circle = data point on flammability boundary; triangle = data point inside boundary (in this case, explosion limits)

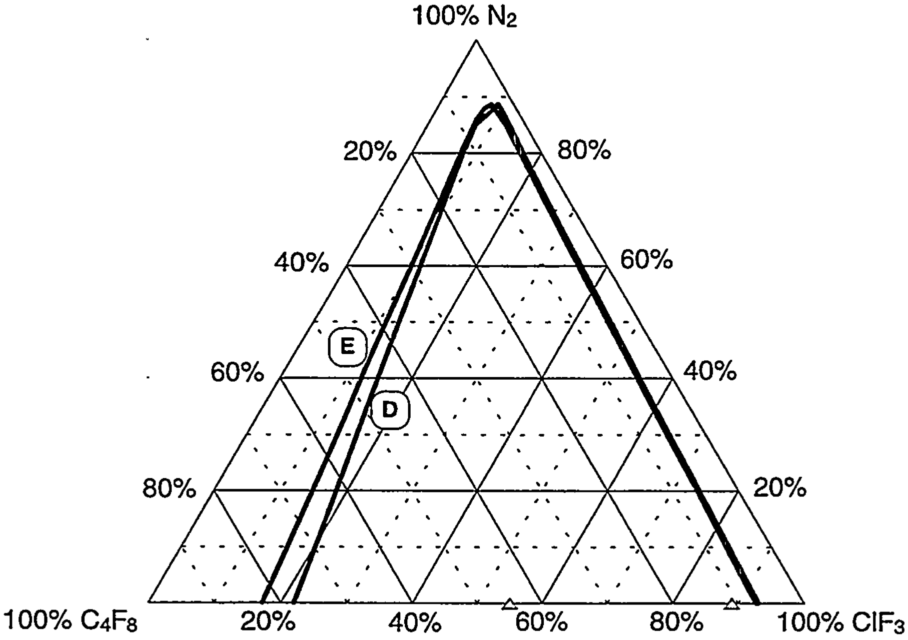


Fig. 4. Flammability boundaries for ClF_3/c-C_4F_8/N_2 mixtures. D = detonation theory prediction; E = equilibrium-based prediction; triangle = data point inside boundary

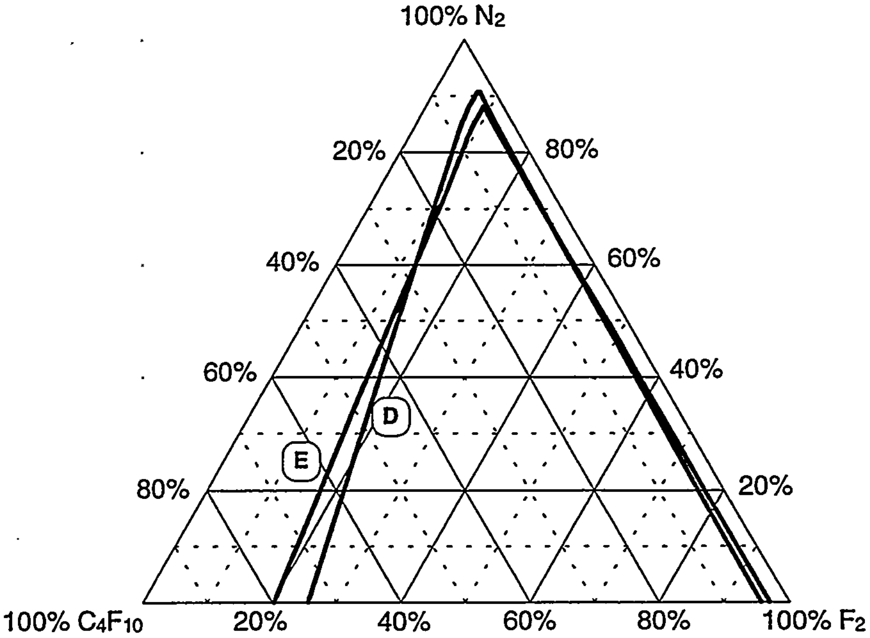


Fig. 5. Flammability boundaries for $F_2/C_4F_{10}/N_2$ mixtures.
D = detonation theory prediction; E = equilibrium-based prediction.

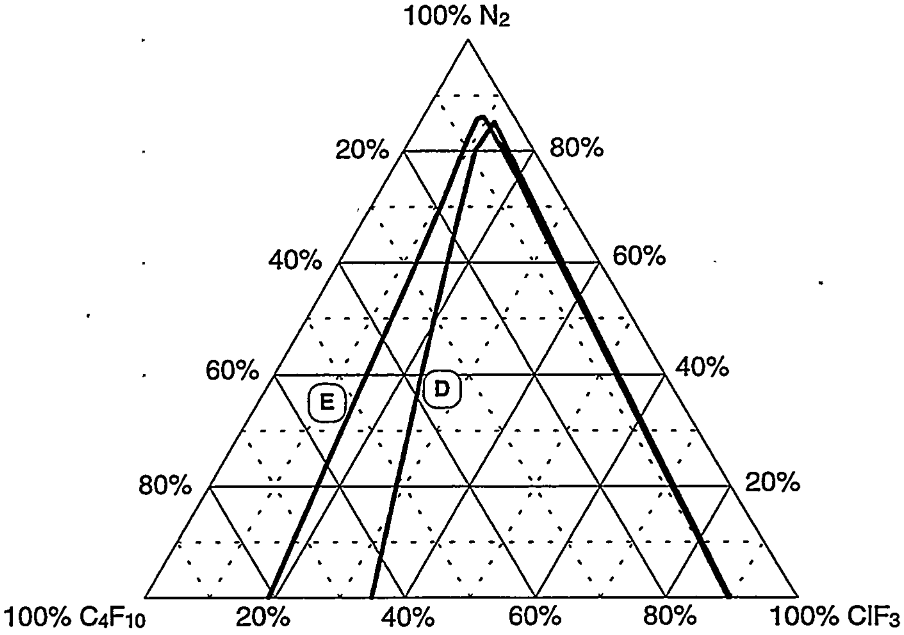


Fig. 6. Flammability boundaries for $ClF_3/C_4F_{10}/N_2$ mixtures.
D = detonation theory prediction; E = equilibrium-based prediction.

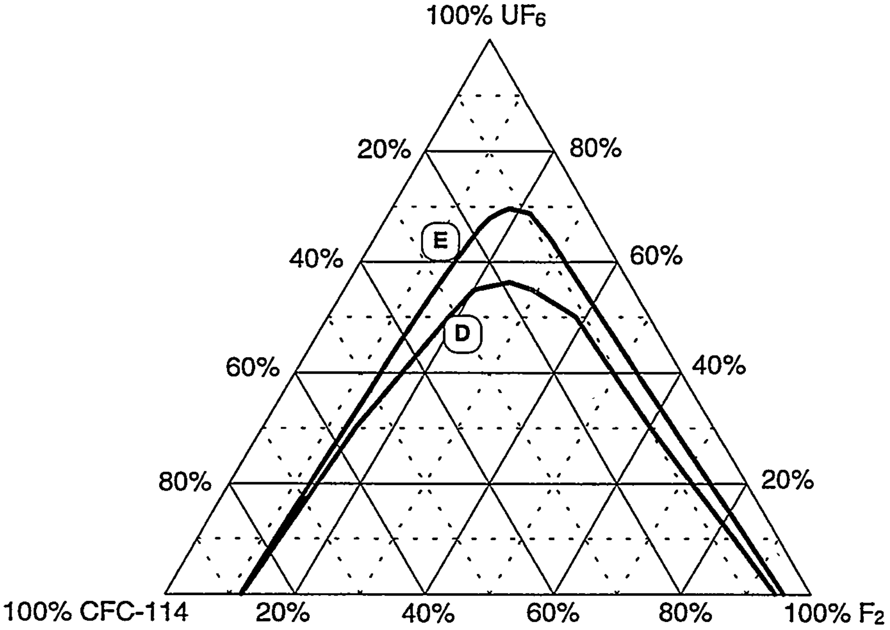


Fig. 7. Flammability boundaries for F_2/CFC-114/UF_6 mixtures.
D = detonation theory prediction; E = equilibrium-based prediction.

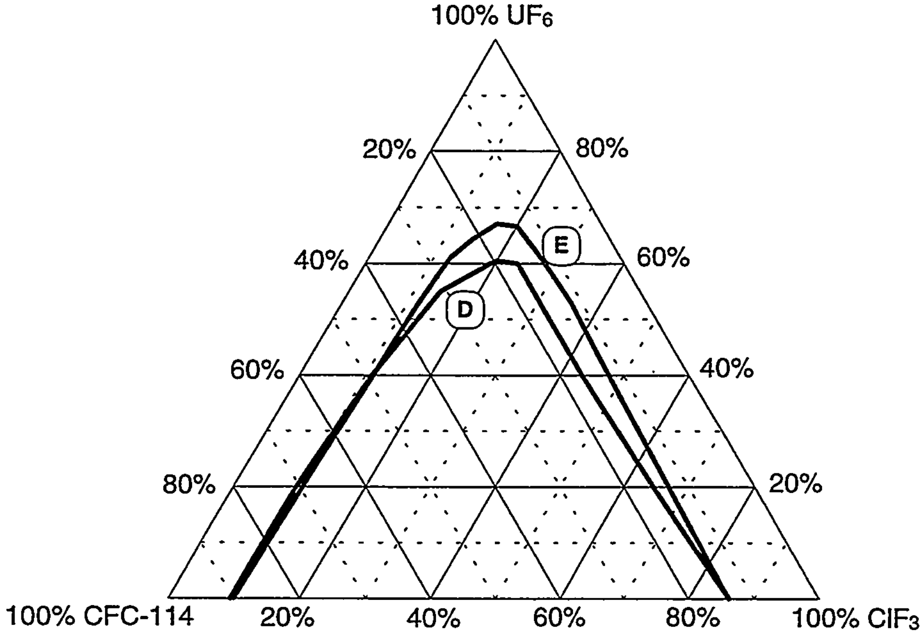


Fig. 8. Flammability boundaries for ClF_3/CFC-114/UF_6 mixtures.
D = detonation theory prediction; E = equilibrium-based prediction.

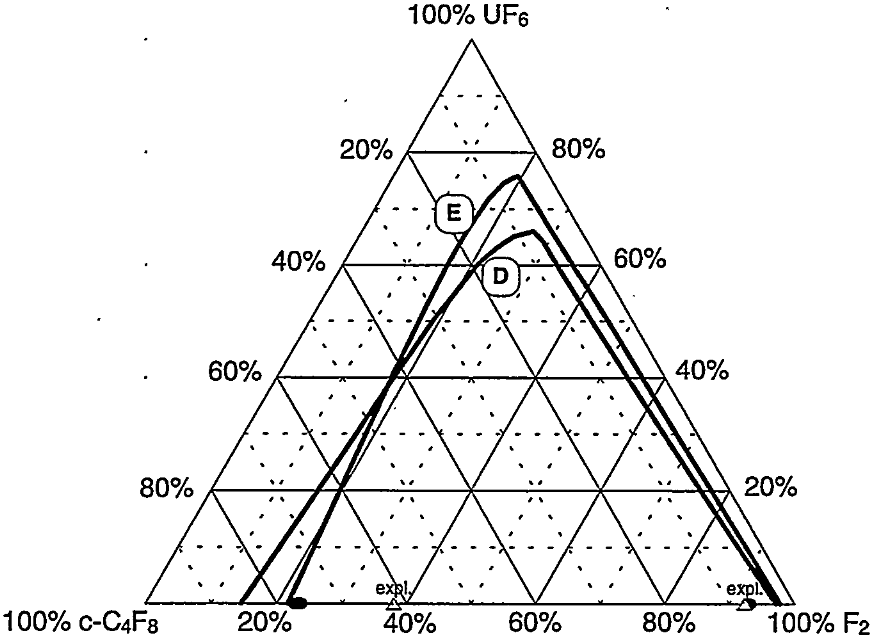


Fig. 9. Flammability boundaries for F_2/c-C_4F_8/UF_6 mixtures. D = detonation theory prediction; E = equilibrium-based prediction; solid circle = data point on flammability boundary; solid triangle = data point inside boundary.

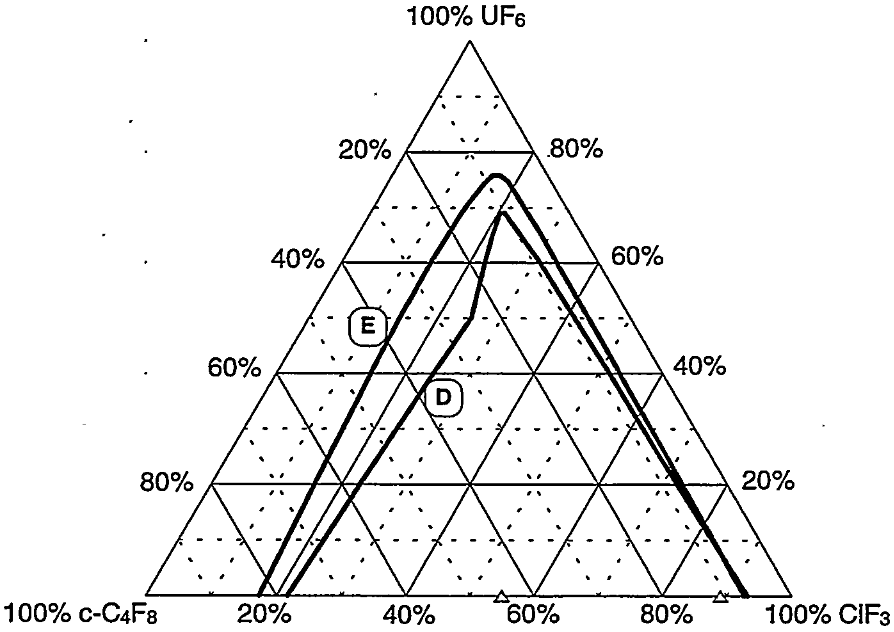


Fig. 10. Flammability boundaries for ClF_3/c-C_4F_8/UF_6 mixtures. D = detonation theory prediction; E = equilibrium-based prediction; solid triangle = data point inside boundary.

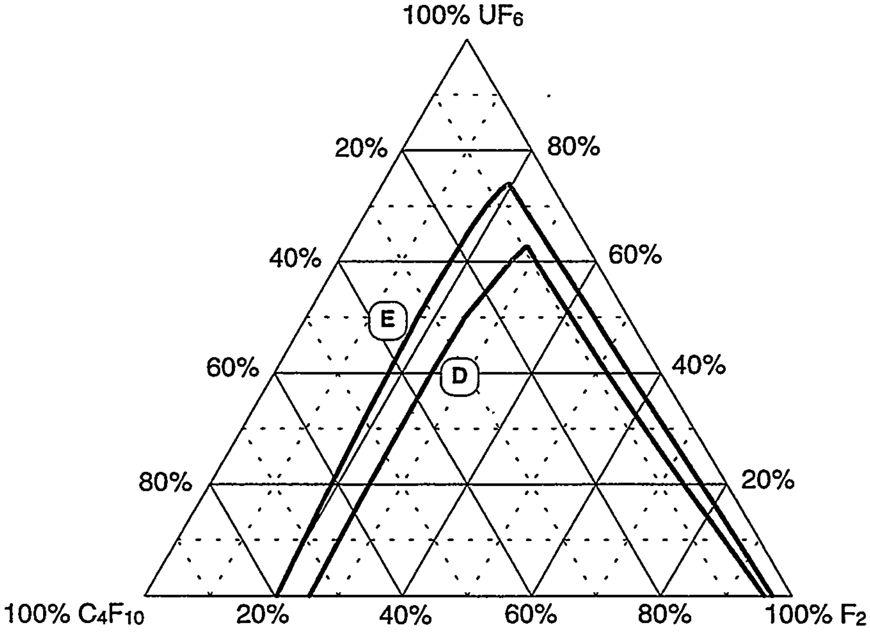


Fig. 11. Flammability boundaries for $F_2/C_4F_{10}/UF_6$ mixtures.
D = detonation theory prediction; E = equilibrium-based prediction

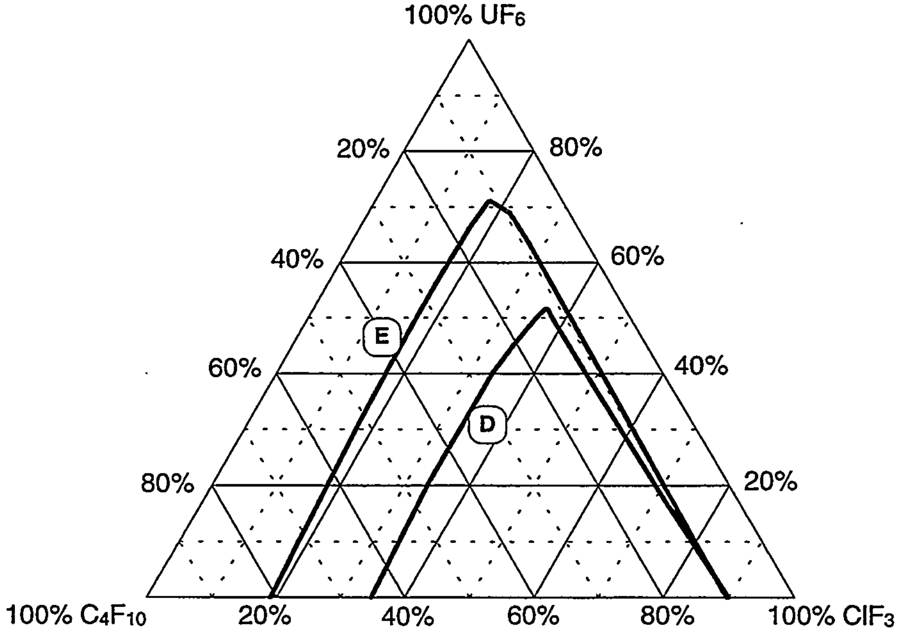


Fig. 12. Flammability boundaries for $ClF_3/C_4F_{10}/UF_6$ mixtures.
D = detonation theory prediction; E = equilibrium-based prediction.

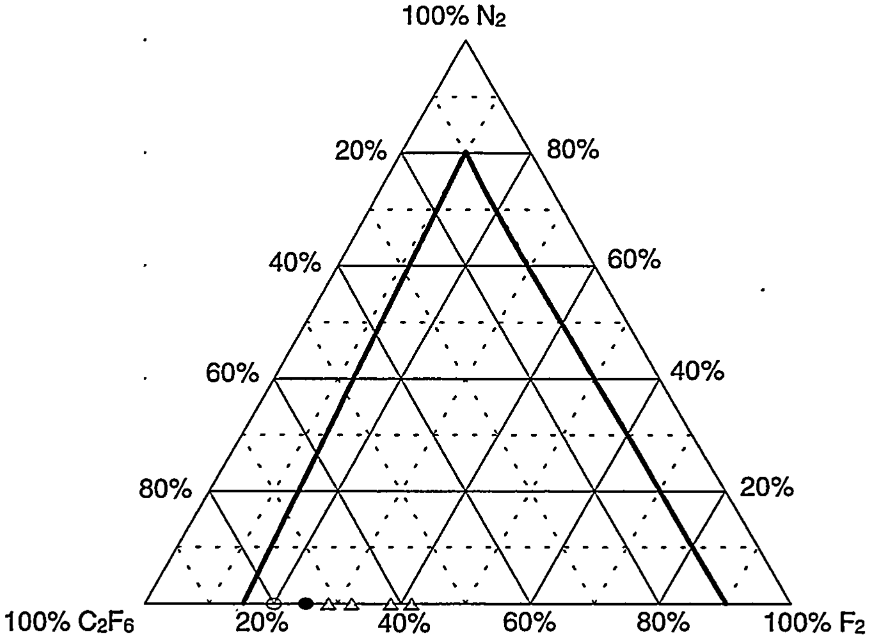


Fig. 13. Flammability boundaries for $F_2/C_2F_6/N_2$ mixtures. Solid line = equilibrium-based prediction; solid circle = experimental data point on flammability boundary; open circle = data point outside boundary; solid triangle = data point inside boundary

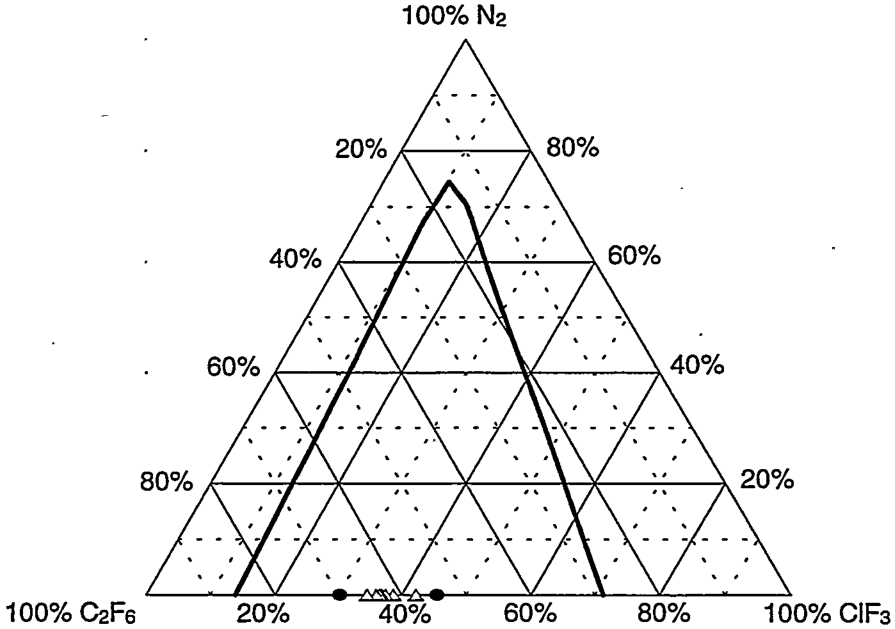


Fig. 14. Flammability boundaries for $ClF_3/C_2F_6/N_2$ mixtures. Solid line = equilibrium-based prediction; solid circle = experimental data point on flammability boundary; solid triangle = data point inside boundary.

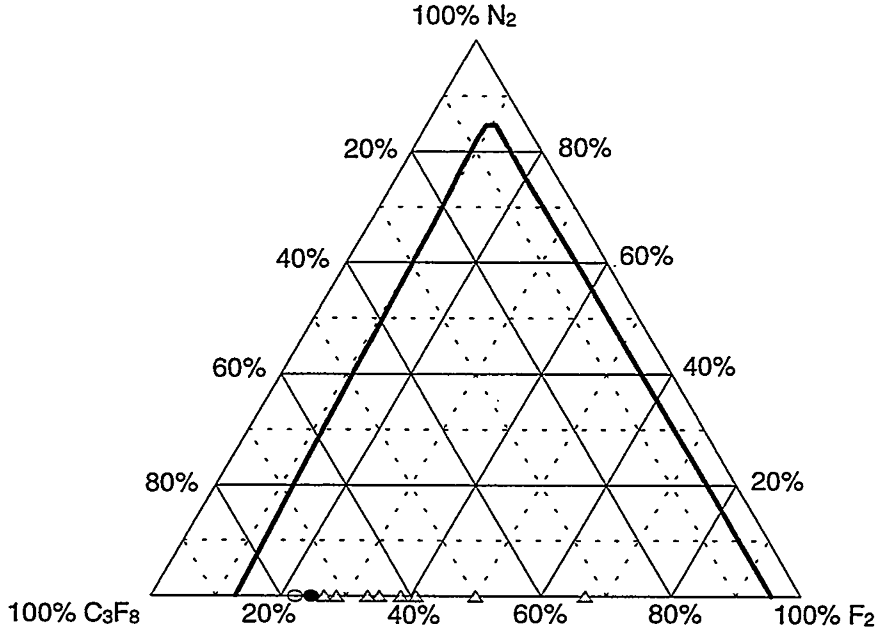


Fig. 15. Flammability boundaries for $F_2/C_3F_8/N_2$ mixtures. Solid line = equilibrium-based prediction; solid circle = experimental data point on flammability boundary; open circle = data point outside boundary; solid triangle = data point inside boundary.

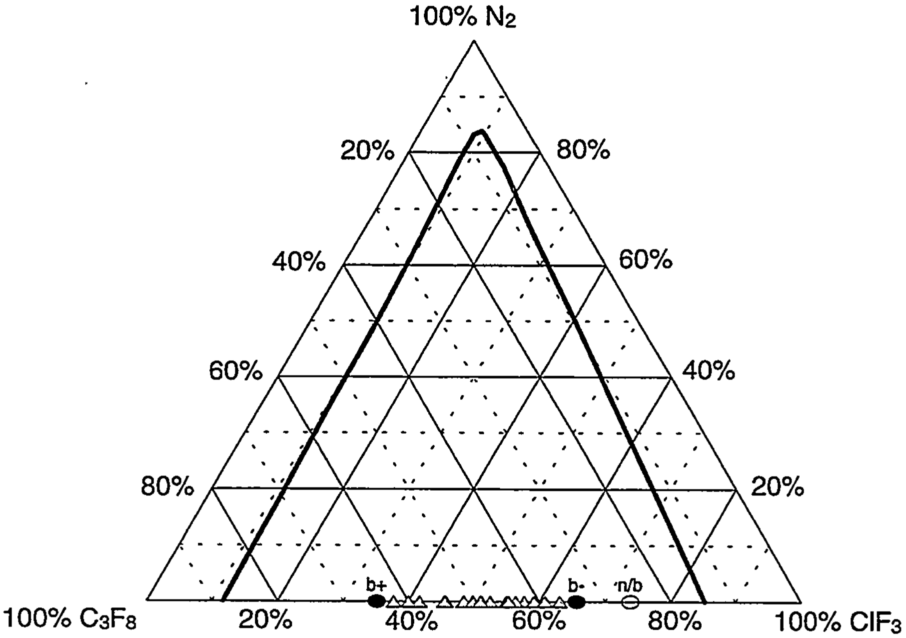


Fig. 16. Flammability boundaries for $ClF_3/C_3F_8/N_2$ mixtures. Solid line = equilibrium-based prediction; solid circle = experimental data point on flammability boundary; open circle = data point outside boundary; solid triangle = data point inside boundary.

available, similar experimental data are listed. Most of the experimental values, however, are from binary mixtures, so there is no guarantee that they would be the minimum concentration in a ternary system. When N_2 is the diluent, the shape of the flammability envelopes typically is such that the minimum fuel or oxidizer concentrations lie in the vicinity of dilute mixtures. When the higher heat capacity UF_6 is the diluent, however, the minimum concentrations usually occur on the no-diluent axis.

Table 3. Minimum flammable concentrations

			Oxidizer			Fuel		
			Expt data[a]	Det. model	Equilibr. model	Expt data[a]	Det. Model	Equilibr.. Model
F_2	CFC-114	N_2	11.0%	5.2%	7.3%	6.0%	3.4%	4.1%
F_2	c-C_4F_8	N_2	***22.9%***	5.1%	7.8%	***7.0%***	1.7%	2.1%
F_2	C_4F_{10}	N_2		6.7%	8.9%		2.3%	2.9%
ClF_3	CFC-114	N_2		3.6%	6.5%		4.0%	6.2%
ClF_3	c-C_4F_8	N_2		7.4%	7.1%	***11.0%***	2.3%	3.0%
ClF_3	C_4F_{10}	N_2		11.1%	8.5%		3.5%	4.5%
F_2	CFC-114	UF_6	***17.5%***	11.9%	11.8%	***8.0%***	5.5%	4.2%
F_2	c-C_4F_8	UF_6	***22.9%***	14.6%	16.3%	***7.0%***	2.8%	2.1%
F_2	C_4F_{10}	UF_6		24.6%	17.4%		4.2%	2.9%
ClF_3	CFC-114	UF_6		9.5%	10.0%		13.9%	11.7%
ClF_3	c-C_4F_8	UF_6		20.2%	13.9%	***11.0%***	6.9%	6.3%
ClF_3	C_4F_{10}	UF_6		33.5%	16.8%		10.1%	8.9%

[a] Experimental data in bold italic are from binary (fuel-oxidizer) mixtures only and are directly comparable to minimum flammable concentrations only if these occur at the 0% diluent boundary (more likely true of UF_6-diluted systems than N_2-diluted systems).

3.3 DISCUSSION

To reiterate, flammability limit predictions are purely empirical. No real theoretical justification exists for either prediction scheme, though some precedent has been established for use of similar empirical schemes in other chemical systems [10, 11]. The models used here are based on correlations and calibrated to the data set shown, so a certain degree of agreement should be expected for the chemical systems used for calibration. The reliability of predictions made for other similar systems is derived solely from the range of systems for which the predictions appear reasonable and on the chemical similarity of the systems in question. Other systems for which we would expect good agreement would be those involving the same fuels and oxidizers but a different diluent, or a mixture of diluents. Similarly, a mixture of fuels or oxidizers from the current set would probably give reliable predictions, but some modification of the models would be needed to handle such mixtures. Similar compounds – for example CFC-115, iso-C_4F_{10}, C_5F_{12}, or c-C_4F_8O (if one could find appropriate thermodynamic data) – would also likely yield flammability boundary predictions that are about as accurate as those presented here. The more dissimilar the compounds and chemistry become, however, the less confidence one would have in predicted flammability boundaries. Hydrofluorocarbons, for example, might have somewhat different combustion chemistry, and thus one should not use these models for such species without some confirmation or recalibration with experimental data.

Some technical limitations exist for the present models. The detonation pressure model, in particular, is set up to operate with a single fuel and oxidizer. Inclusion of another oxidizer or fuel in the starting mix for any of the versions of these models results in the new reactant being treated as an inert diluent. It would not be at all straightforward to attempt to modify the spreadsheets to include mixed fuels and/or oxidizers. The equilibrium-based model, as currently constituted, also assumes a single fuel and oxidizer. This limitation manifests itself only in the "stoichiometry parameter" provided as part of the list of data sets to run. This number is the ratio of oxidizer to fuel needed to completely react the fuel without excess of fuel or oxidizer. For any particular composition of mixed fuels and oxidizers, such a value can be readily defined. To do so for a large number of points in which the ratios of the various fuels or oxidizers change could be cumbersome, and a more automated process could be developed.

Reaction-chamber size effects are not captured by any of the data used in calibration of the flammability limit models or in the functional form of the model. Consequently, phenomena such as quench distance and lower pressure limit of flammability (a related factor) will not be predicted. These phenomena are probably not of great relevance to the intended use of these models.

The detonation pressure model is based on a well-developed and accepted theory of shock propagation and combustion and rests on that theory rather than on directly applicable experimental data for fluorocarbon-fluorine explosions. For the results to have a degree of validity, however, it is necessary to choose an appropriate set of chemical reactions. It is not necessary that the reaction chemistry be completely exact, but the energetics of the reactions chosen should be approximately the same as the reactions that actually occur in combustion. The results, however, will only be as accurate as the accuracy of the chemistry assumed. The models as presently constituted do not have a provision for dissociating reaction products and thus may slightly overestimate pressures. At the temperatures and times appropriate to the presumed detonation, considerable dissociation of fluorocarbons can occur, major radical species being CF_2 and CF_3. Even at lower temperatures, ClF_3, if in excess, will likely dissociate to ClF and F_2. Any dissociation of this sort will lower the temperature of the gas mix but increase the number of moles of gas, compensating factors that, however, would not cancel. To properly treat dissociation would require a much more detailed treatment of the kinetics of combustion than is contained in either of these models. An approximate treatment including dissociation could be carried out by calculating the appropriate thermodynamic equilibrium at shock temperatures, rather than, as at present, assuming that a specific set of reactions go to completion.

The detonation pressure model in general predicts what will happens assuming that one or two reactions have initiated, propagated, and accelerated to fully developed shock conditions. It does not, except in extreme cases, tell *if* the system can actually accomplish these events successfully. In extreme conditions, the model may yield results in which the impulse is lower than the detonation pressure. In such cases, gas movement is calculated to be in a direction opposite to the direction of propagation of the shock, hardly a condition conducive to development of a shock. The true boundaries of explosivity of the gas mixture lie well beyond such conditions, however. The model will compute detonation pressures for conditions where, in fact, no detonation would actually occur in a practical case. The flammability prediction in the detonation pressure model spreadsheets does not derive from the detonation theory itself, but is an empirical correlation based on the thermochemistry of the system.

The 1992 explosion pressure models used a subsonic flame propagation theory to estimate pressure of a gas mixture as it burns in a closed vessel. That model of combustion computes pressure as a function of the fraction of gas burned but does not compute the rate of flame propagation during that process. To do that would require calibration with experimental flame speed data. An approximation was employed to estimate the potential detonation (i.e., fully developed shock) pressure from the final gas pressure. Again, no real criterion existed in that model (nor in the present versions) to determine *if* such a detonation would occur for a given gas mix. The potential detonation pressure was subsequently used in various analyses of GDP systems to evaluate safety or potential hardware integrity in gas explosion scenarios. A factor not included in those analyses is the "impulse," which is a pressure-like term that includes not only the detonation pressure (the local pressure in the shock wave) but also the effect of the forward motion of that shock wave.

In interpreting effects of potential detonations, it is important to consider the short durations involved. Assuming it forms in the first place, the shock wave may be traveling at several hundreds of meters per second, but the zone of combustion may be on the order of millimeters broad, and the postshock high pressure region some multiple of this. The pressures generated may be very high, but are present for a very short time, which limits the energy that can be transferred to the walls confining the explosion. Naturally, treating the detonation pressure (or impulse) as though it were a static pressure is conservative, but may well be excessively so. If such a treatment suggests that costly counter-measures should be taken, it may be wise to examine the time-dependent effects more closely.

During the modification and development of the models discussed here, it became apparent that some of the weaknesses and limitations of the two models could be minimized by a comprehensive approach combining elements of each. Both models, but more particularly the detonation pressure model, are limited to consideration of gas mixtures containing a single fuel and single oxidizer. In real applications, it is likely that a combination of such species will be present. A second problem with the detonation pressure model as currently constituted is the difficulty of considering dissociation and other high temperature chemical effects. These difficulties could in large measure be eliminated by use of the thermodynamic equilibrium calculation for determining the reaction endpoint rather than resorting to specific defined reactions. Although a combined model is quite practical, it exceeds the scope of the present effort and is the subject of possible future development.

4. CONCLUSIONS

The 1992 detonation pressure model has been revised, updated, and documented. The current versions are applicable to any oxidizer/fuel ratio of gas mixtures containing F_2 or ClF_3 reacting with any one of CFC-114, c-C_4F_8, or C_4F_{10}. The model directly uses a well-established theory of gas detonation to calculate the pressure that would occur in the shock if the combustion were to accelerate to a fully developed shock. It also calculates the constant volume adiabatic temperature of the mixture upon reaction, without reference to combustion dynamics. An empirical correlation between adiabatic temperature and gas flammability is used to make a prediction as to the flammability of the mixture under consideration.

A second 1992 model, which predicts flammability limits based on the thermodynamic equilibrium of a gas mixture, has also been updated and documented.

Results were presented for predictions of flammability limits for 16 fuel/oxidizer/diluent combinations, with the mixtures drawn from those combinations of specific interest to gaseous diffusion plant applications or for similar systems for which experimental flammability limit data are available.

APPENDIX A

OPERATION AND DESCRIPTION OF DETONATION THEORY MODEL

A.1 INTRODUCTION

The detonation theory models, descended from a series of spreadsheets developed by E. J. Barber, Jr., retain the basic spreadsheet format, but are much altered in layout and operation. There are six versions of the model, one for each fuel/oxidizer combination. These are named F_114, L_114, F_318, L_318, F_3110 and L_3110, where F_xxx uses F_2 as the oxidizer and L_xxx uses ClF_3, and 114, 318, and 3110 use CFC-114, c-C_4F_8, and C_4F_{10}, respectively, as the fuels. The spreadsheets were developed using Corel's Quattro Pro version 8 but have been converted and tested in Lotus 1,2,3 (version 5) and Microsoft Excel 97. A few formulae had to be changed, but there is no difference in operation between the various commercial spreadsheet versions.

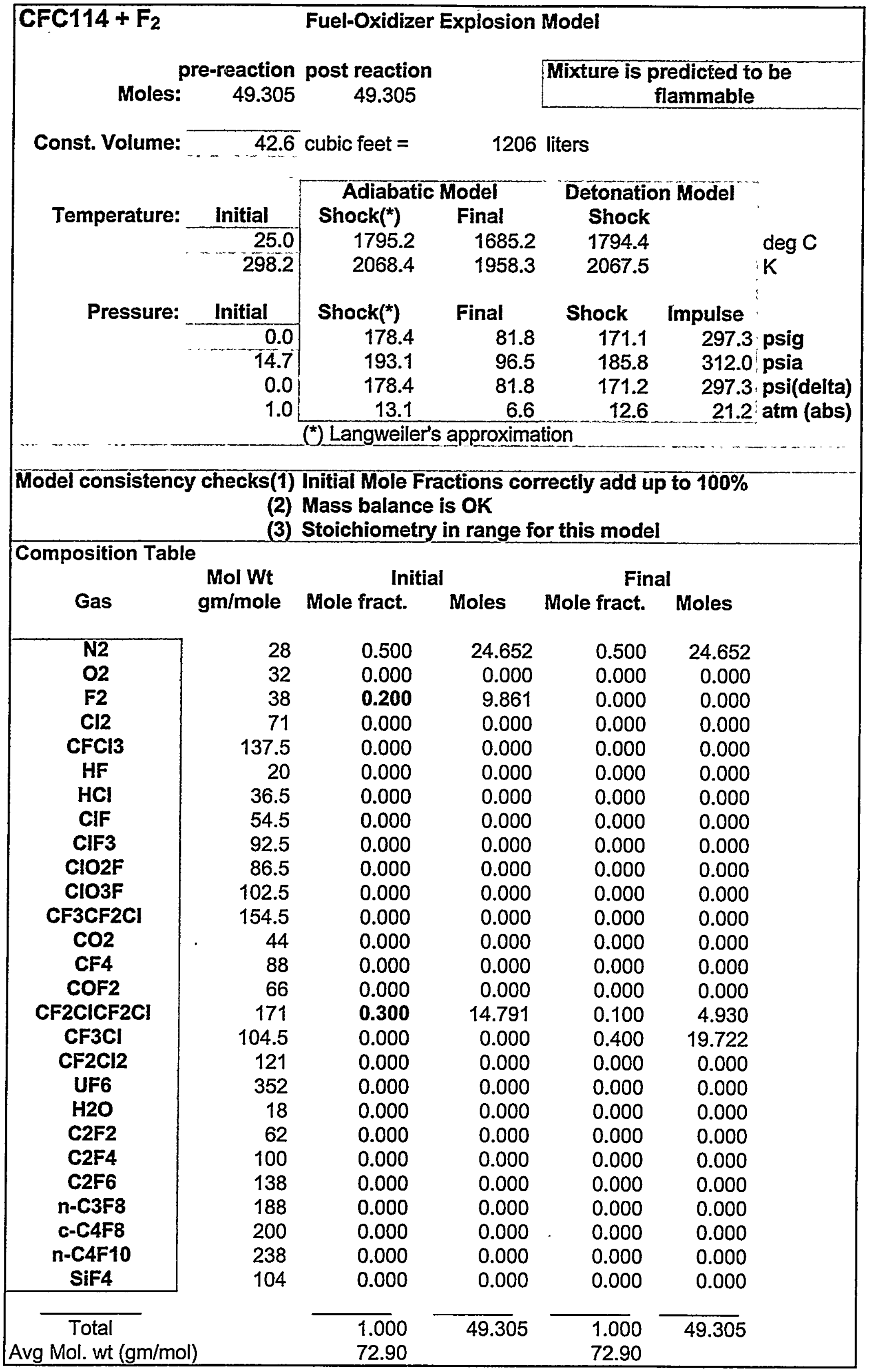
A.2 OPERATION

This section describes the normal operation of the spreadsheet models. Examples will be taken from the F_114 version. All formulae necessary to calculate results from user-supplied inputs are directly programmed into the spreadsheet. There is no need to run macros or resort to external calculations to obtain model results. As long as the user's commercial spreadsheet software is set up to automatically recalculate a spreadsheet upon input of new cell values (a normal default condition for spreadsheets), a change in any input parameter will appropriately alter the model results.

Many cells in the spreadsheet are color coded to assist the user in model operation. Items in *yellow* are intended to be the primary input parameters for the model. These include the total system volume, the initial temperature, initial pressure, and the initial mole fraction of each starting material. Cells in *green* are those which might need to be altered only if the fundamental structure of the spreadsheet were changed. Such a change might be desired if a different oxidizer or fuel were to be used or if an alternate set of characteristic chemical reactions were to be used. Other cell colors are present solely for emphasis.

Exhibit A.1 is a display of the primary input and output region of the model (the upper left corner of the first sheet). The upper portion is the summary table, containing the physical parameters comprising the main input and output of the model. There is a section for number of moles (that is, gm-moles) of gas, the volume, the temperature, and the pressure, the latter two parameters being presented in several units. Under temperature and pressure, there are two sets of two columns of results, one for the constant volume adiabatic calculation and the other for the detonation theory model. Under the adiabatic model, the "Final" entry is the actual result of calculating the adiabatic constant volume end point for the reactions and quantities specified.

Exhibit A-1: Screen Display of Summary Section of F_114



CFC114 + F_2 **Fuel-Oxidizer Explosion Model**

	pre-reaction	post reaction
Moles:	49.305	49.305

Mixture is predicted to be flammable

Const. Volume: 42.6 cubic feet = 1206 liters

		Adiabatic Model		Detonation Model	
Temperature:	**Initial**	**Shock(*)**	**Final**	**Shock**	
	25.0	1795.2	1685.2	1794.4	deg C
	298.2	2068.4	1958.3	2067.5	K

Pressure:	**Initial**	**Shock(*)**	**Final**	**Shock**	**Impulse**	
	0.0	178.4	81.8	171.1	297.3	**psig**
	14.7	193.1	96.5	185.8	312.0	**psia**
	0.0	178.4	81.8	171.2	297.3	**psi(delta)**
	1.0	13.1	6.6	12.6	21.2	**atm (abs)**

(*) Langweiler's approximation

Model consistency checks(1) Initial Mole Fractions correctly add up to 100%
(2) Mass balance is OK
(3) Stoichiometry in range for this model

Composition Table

Gas	Mol Wt gm/mole	Initial Mole fract.	Initial Moles	Final Mole fract.	Final Moles
N2	28	0.500	24.652	0.500	24.652
O2	32	0.000	0.000	0.000	0.000
F2	38	**0.200**	9.861	0.000	0.000
Cl2	71	0.000	0.000	0.000	0.000
CFCl3	137.5	0.000	0.000	0.000	0.000
HF	20	0.000	0.000	0.000	0.000
HCl	36.5	0.000	0.000	0.000	0.000
ClF	54.5	0.000	0.000	0.000	0.000
ClF3	92.5	0.000	0.000	0.000	0.000
ClO2F	86.5	0.000	0.000	0.000	0.000
ClO3F	102.5	0.000	0.000	0.000	0.000
CF3CF2Cl	154.5	0.000	0.000	0.000	0.000
CO2	44	0.000	0.000	0.000	0.000
CF4	88	0.000	0.000	0.000	0.000
COF2	66	0.000	0.000	0.000	0.000
CF2ClCF2Cl	171	**0.300**	14.791	0.100	4.930
CF3Cl	104.5	0.000	0.000	0.400	19.722
CF2Cl2	121	0.000	0.000	0.000	0.000
UF6	352	0.000	0.000	0.000	0.000
H2O	18	0.000	0.000	0.000	0.000
C2F2	62	0.000	0.000	0.000	0.000
C2F4	100	0.000	0.000	0.000	0.000
C2F6	138	0.000	0.000	0.000	0.000
n-C3F8	188	0.000	0.000	0.000	0.000
c-C4F8	200	0.000	0.000	0.000	0.000
n-C4F10	238	0.000	0.000	0.000	0.000
SiF4	104	0.000	0.000	0.000	0.000
Total		1.000	49.305	1.000	49.305
Avg Mol. wt (gm/mol)		72.90		72.90	

The "Shock(*)" column gives an approximation to the shock pressure and temperature should the mix proceed to a fully developed shock. This temperature and pressure are derived from Langweiler's approximation, which is the approximation used by Barber in the 1992 versions of the model. If the approximation were perfect, the results should agree with the "Shock" column under the "Detonation Model". In the example shown in Exhibit A.1, the agreement is not bad (100 psia for the approximation versus 92 psig for the explicit theoretical calculation).

In the Detonation Model section, shock temperature and pressures are displayed. These are the conditions calculated to exist in the compressed gas of a fully developed shock wave. In addition to being compressed, the gas in the shock wave will be moving in the direction of propagation of the wave. The momentum of the moving gas leads to an additional force on any surface not parallel to that motion. The "Impulse" is the force exerted on a surface perpendicular to the direction of motion of the shock wave and is due to the sum of the momentum term and the shock pressure.

In the upper right section of the summary block is a prediction of the flammability of the present mixture. This is based on the empirical correlation between adiabatic temperature and flammability discussed elsewhere in this report.

Immediately below the summary block are three diagnostic messages. The first indicates whether or not the user-specified mole fractions correctly add up to 100% and is the diagnostic most likely to be triggered. The second and third relate to mass balance and allowable ranges of fuel-to-oxidizer ratio. A comparison is made of mass balance (initial to final) for F, Cl, and C. An error in mass balance will generally occur only if the chemical reactions have been altered and one or more is incorrectly balanced. The present spreadsheets allow any ratio of oxidizer-to-fuel from 0 to infinity, so the stoichiometry range message, in practice, will be triggered only if a negative mole fraction is entered. In principle, an altered version of the spreadsheet might restrict the allowable stoichiometry range more than the current versions.

The next section down is the "Composition Table." It contains the initial mole fractions of many possible species. The user must enter the appropriate values for the desired species in this (yellow-highlighted) column, and the total must add to 1 (i.e., 100%). The fuel and oxidizer for the current spreadsheet are in boldface. Only these two species will react in the current model, regardless of the chemical reactivity of other species. For example, in the illustration shown, it would be possible to specify some quantity for the initial concentration of, for example, c-C_4F_8, but in this version of the spreadsheet, it would be treated merely as an inert diluent.

The remaining sections of the spreadsheet, while essential to the functioning of the model, need not be viewed or altered by the user to operate the model. Operation of the model simply consists of entering the desired physical and composition parameters into the appropriate (yellow highlighted) cells. The results will be automatically calculated whenever an input parameter changes.

A.3 LAYOUT

This section of the appendix describes the regions of the spreadsheet and their general functions. The operational portion of the model is all on sheet A, and those used for normal operation have been described previously. Sheet B is purely informational and contains descriptive and background material on the basis of the model.

The Composition Table contains the initial and final quantities for all gaseous species. In addition to the initial mole fractions discussed previously, the table also contains values for the initial number of moles and the final number of moles and mole fractions. To the right of the summary table are tables depicting the allowable reactions in the model. The Reaction List indicates the reactions considered, sorted in order of oxidizer-to-fuel ratio. This list is for information only. The section headed Selection of Active Reactions . . . chooses the appropriate one or two reactions from the reaction list which will accommodate the initial ratio of reactants, calculates the quantity of excess fuel or oxidizer (if any), and apportions the fuel and oxidizer between the two reactions if two are to be used.

Below this is the Reaction Stoichiometry Table, which indicates the number of moles of each species either consumed (negative entries) or produced (positive entries) *per mole of fuel reacted* in each available reaction. To the right is the Reaction Matrix, which calculates the number of moles reacted according to each operative chemical reaction and also calculates the heat of reaction and an adjustment if the starting temperature is other than 298.15 K.

Further to the right is the Thermodynamics Property Table, which contains values for the enthalpy of formation, entropy (not actually used in this version of the model), and coefficients for a polynomial fit of C_P data as a function of temperature. Above this table are two rows containing the weighted sum of the parameter values for the initial and the final product mixes.

To the right is the Mass Balance Table, which is used merely as a check to see that the starting and ending states preserve each element. If a mass balance error occurs, most likely it will be because a new reaction or species was entered with incorrect mass balance or stoichiometry coefficients.

At the left, below the Composition Table, are the intermediate values used to calculate the results of the Adiabatic Reaction Model, and below that are the intermediate values for calculating the results of the Detonation Theory Model. The spreadsheet follows the mathematics of each model, as discussed in the main body of this report.

A.4 MODIFYING THE MODEL

It may prove desirable to modify the models, perhaps to include different reactions, to add different diluents, or to create new versions which use different fuels or oxidizers. An attempt has been made to define those sections which would need to be altered to make such modifications and to modularize the layout as much as possible to facilitate modification.

A.4.1 Adding and Deleting Reactions

Reactions must be listed in stoichiometry order (i.e., in order of increasing oxidizer-to-fuel ratio) The text entry in the Reaction List is for convenience only. The Reaction Stoichiometry Table entries should list the number of moles of fuel and oxidizer in each reaction equation and also the number of moles of each product (positive) or reactant (negative) in the reaction equation. The coefficients used in the reaction equation must be expressed in a "per-mole-of-fuel" basis. Thus, for all reactions the entry for the fuel will be "- 1." For unused spaces in the Reaction Stoichiometry Table, enter 9E99 for the fuel moles, 1 for oxidizer moles, and all zeroes in the coefficients in the body of the table. As long as you restrict the series to the five possible reaction entries available, sums and table definitions should function properly as reactions are added or deleted. If more than five reactions are needed, the table must be expanded, and array bounds will have to be checked in formulae using the Stoichiometry Table entries.

If the fuel or oxidizer species change, you must alter the references in the Selection of Active Reactions . . . table (just above the Stoichiometry Table). Change "Initial/$N_{oxidizer}$" and/or "Initial/N_{Fuel}" cells to refer to the proper entry in the "Initial Moles" column (Column D).

A.4.2 Adding / Deleting Species

Chemical species data and formulae are all contained in a contiguous set of rows (rows 27 to 53 as this is being written, but that could change with species addition or deletion). No other formulae intrude in this region. Therefore, deleting a species can be done merely by deleting its row. Avoid deleting the first or last row, however, as they define the limits of sums and vector products used throughout the spreadsheet. Inserting a new species can be done by inserting a row, copying the entire contents of an adjacent row into the new blank one (this will capture all arithmetic formulae in the row), then entering the appropriate species-specific data: name; stoichiometry coefficients (if it participates in reactions) in the Reaction Stoichiometry Table; enthalpy of formation and C_P coefficients in the Thermodynamic Properties Table; mass balance coefficients in the Mass Balance Table. $C_P(T)$ coefficients must derive from a fit of $C_P(T)$ to the equation

$$C_P = a + e / T + e / T^2 + e / T^3 + e / T^4 \quad .$$

ΔH_f and C_P must be in units of cal/mole (...per K, for C_P). The Mass Balance Table is used to perform limited before-vs.-after mass balance checks on selected elements (at present, F, C, and Cl). If a new species is added which will participate in reactions, the values for its chemical formula must be entered in this table.

APPENDIX B

UTILITIES FOR AUTOMATION OF EQUILIBRIUM-BASED FLAMMABILITY LIMIT MODEL

The equilibrium-based model presented in the main text for prediction of flammability boundaries is essentially conceptual in nature. For any given composition, the model simply predicts a threshold temperature as a function of composition based on empirically derived parameters. If the equilibrium adiabatic temperature of the mixture, as calculated from available thermodynamic data on products, reactants, and diluents, exceeds this threshold temperature, the mixture is predicted to be flammable. Using the conceptual model of the equilibrium-based flame limit, one can make a prediction of flammability for a given mixture by

(1) manually calculating the threshold temperature using the formula given in the main text, then

(2) calculating the adiabatic temperature of that mixture equilibrium when it reacts to equilibrium.

The conceptual model, or rather its calibration parameter set, is based on certain information (i.e., particular experimental data for mixtures known to burn and thermodynamic data for reactants and possible reaction products involved) but is not really tied to any particular software. Certain software was, however, used to expeditiously carry out the numerous calculations involved in model calibration and mapping of predicted flammability envelopes. The thermodynamic data used in these calculations were discussed in the main body of the report. Thermodynamic equilibria are calculated using the program SOLGAS (specifically, version 3.02b5, as discussed in ref. 16). SOLGAS finds the equilibrium for a chemical system defined by user-specified starting material quantities, initial temperature, final temperature, and pressure. It uses thermodynamic information (heats of formation, heat capacities, and entropies) for each chemical species which might participate as a reactant or product, calculates the equilibrium state of the system, and computes the quantity of heat released or absorbed in the process. The adiabatic temperature of a mixture reacting to its equilibrium state can be found manually by changing the final temperature until the net heat evolution is zero. This may be adequate for one or a few mixtures but is tedious if many need to be found

B.1 ADIAB95.EXE

The process of finding an adiabatic temperature for a gas mixture using SOLGAS is automated using the utility program ADIABAT.EXE. ADIABAT is a "driver" for SOLGAS, that is, a program that, within limits, controls and runs SOLGAS to simulate certain (repetitive) operations that a human user might perform. Operation of ADIABAT was discussed in the 1995 release of SOLGAS [16]. That 1995 version required minor modification to operate satisfactorily under Windows 95, and the modified version, ADIAB95.EXE, is available from the author and has been provided to technical contacts at the GDPs along with other software related to this report. ADIAB95 is written in Borland, Inc.'s Turbo Pascal v 6.0, compiled for IBM PC compatible machines. It is a DOS program, but generally is run in a DOS window under Windows 95. The basic function and operation of ADIAB95 has not changed from that discussed in ref. 16 and will not be repeated in detail here. However, a very brief description of operation follows.

(1) Assemble the appropriate files in one folder. These are:
  (a) ADIAB95.EXE
  (b) SOLGAS.EXE (a renamed copy of SOL302b5.EXE)
  (c) Thermodynamics data file suitable for SOLGAS and for the problem at hand
  (d) Driver control file

(2) Run ADIAB95.EXE (e.g., double click its icon).

If the files were properly set up, ADIAB95 should repeatedly run SOLGAS, altering the starting temperature for the first mixture specified in the driver control file until the adiabatic temperature of that mixture is found. It will then repeat the process for each succeeding mixture listed in the control file.

The format of the thermodynamics data file is described in ref. 16. Of course, the fuel and oxidizer(s) in question presumably will be listed as starting materials. A sample file is shown in Exhibit B.1.

The driver control file used by ADIAB95.EXE is a plain text (ASCII) file comprising a title line (which will be ignored, but allows the user to label columns or include a title or description) followed by a series of data lines, each one of which describes the parameters for a single gas mixture. The entries on each line are, in order, as follows::

(a) Control parameter number, indicating the parameter to be varied as the adiabatic temperature is sought. For purposes here, this should be "0" (zero), indicating that the temperature is to be varied.
(b) Starting temperature (K).
(c) Fixed pressure (bar)
(d) Initial quantity of first starting material indicated in thermodynamics data file (i.e. those indicated by an asterisk (*) in the first column). In the file shown in Exhibit B-1, this would be the species N2(g).
(e), (f), etc. Initial quantity of succeeding starting materials

A sample control file is shown in Exhibit B-2

Exhibit B.1 - Sample data file used by SOLGAS

```
TITLE  1999 campaign -  - adiabatic calculation for flame limit data
T= 373              dHf         S     Cp a         Cp b         Cp c         Cp d        Cp e
*G N2(g)     N2            0  191.609   32.010   2.429E-03  -2.365E-07  -1.724E+06  4.238E+08 ;JANAF 86
*G F2(g)     F2            0  202.789   38.954   6.315E-04  -3.980E-07  -2.067E+06  4.131E+08 ;JANAF 86
 G ClF(g)    ClF      -50292  217.938   43.463  -7.954E-03   2.708E-06  -1.947E+06  3.346E+08 ;JANAF 86
 G ClF3(g)   ClF3    -158866  281.600   82.688   3.510E-04  -6.093E-08  -2.645E+06  2.885E+08 ;JANAF 86
*G CFC114(g) C2F4Cl2 -890400  370      186.485  -2.440E-03   2.484E-07  -1.571E+07  2.962E+09 ;NBS 82
 G CFC115(g) C2F5Cl -1094116  357.8    181.823  -1.943E-03   2.124E-07  -1.560E+07  2.671E+09 ;
 G nC4F10(g) C4F10  -2140000  481      353.469  -9.518E-03   1.080E-06  -2.691E+07  3.980E+09 ;DAH 90
 G cC4F8(g)  C4F8   -1472768  400      313.511  -1.508E-02        0     -3.498E+07  6.374E+09 ;HD 55 (dHf)
 G CF4       CF4     -933199  261.419  100.463   3.860E-03  -4.525E-07  -6.584E+06  8.909E+08 ;JANAF 86
 G CF        CF       255224  213.033   36.987   4.089E-04   2.052E-08  -2.102E+06  4.417E+08 ;JANAF 86
 G CF2       CF2     -182004  240.833   57.622  -2.669E-04   2.616E-07  -4.351E+06  8.055E+08 ;JANAF 86
 G CF3       CF3     -470282  265.082   77.336   2.945E-03  -3.455E-07  -4.696E+06  6.497E+08 ;JANAF 86
 G C2F2      C2F2      20920  244.060   83.565   1.690E-03  -1.858E-07  -6.507E+06  1.227E+09 ;JANAF 86
 G C2F4      C2F4    -658562  300.015  120.585   6.123E-03  -7.077E-07  -6.797E+06  9.132E+08 ;JANAF 86
 G C2F5      C2F5    -896000  348.691  155.578   1.168E-03  -1.332E-07  -1.375E+07  2.434E+09 ;JML 83
 G C2F6      C2F6   -1343901  332.185  171.981   3.605E-03  -4.369E-07  -1.103E+07  1.487E+09 ;JANAF 86
 G C3F8      C3F8   -1698704  360.00   263.147  -5.148E-03   5.167E-07  -3.202E+07  5.723E+09 ;EAF 64(dHf)
 G CF2Cl2    CF2Cl2  -491620  300.897  104.34    1.929E-03  -2.280E-07  -5.012E+06  6.362E+08 ;JANAF 86
 G CF3Cl     CF3Cl   -707933  285.353  102.521   2.839E-03  -3.340E-07  -5.778E+06  7.594E+08 ;JANAF 86
 G CFCl3     CFCl3   -288696  309.735  105.963   1.111E-03  -1.322E-07  -4.216E+06  5.110E+08 ;JANAF 86
 G Cl(g)     Cl       121302  165.189   22.660  -7.947E-04   8.448E-08   346700    -1.208E+08 ;JANAF 86
 G Cl2(g)    Cl2           0  223.079   32.769   4.193E-03  -5.560E-07   8.667E+05 -2.631E+08 ;JANAF 86
 G F(g)      F         79390  158.750   20.915  -5.826E-05   6.426E-09   5.029E+05 -1.012E+08 ;JANAF 86
```

Exhibit B.2. Sample control file for ADIAB95.EXE

```
Ctrl  T(K)    P(bar)  Xi(dil)  Xi(Ox)   Xi(FC)   System: N2-F2-114
0     1500    1.013   0.75     0.19     0.06
0     1500    1.013   0.70     0.24     0.06
0     1500    1.013   0.55     0.38     0.07
```

Upon running ADIAB95, the user will be asked for the names of the thermodynamics data file, the control file, and a name for an output file. Following these questions, the program will run through the cases specified. The output file contains the input parameters (pressure, starting material quantities) and final temperature of each mixture successfully run. The file is a text file structured in a format suitable for import into commercial spreadsheet programs, in "quote and comma delimited," also known as "comma separated variable" format.

B.2 FLAME4d.EXE

ADIAB95 is suitable for producing a list of adiabatic temperatures which can be compared with the empirical threshold temperature formula applied to those compositions to allows one to determine if a large set of mixtures is predicted to be flammable. It does not, however, directly seek points on the predicted flammability envelope. To automate this process, the program FLAME4d.EXE was developed. Its operation is very similar to ADIAB95, but it actively seeks compositions whose adiabatic temperatures match the threshold temperature function for that mixture. The threshold function is an empirical fit of various fluorocarbon and chlorofluorocarbon flammability limit data and is designed to predict the "ignition temperature" as a function of composition. The program varies the starting quantity of one species, as designated by the user's control file, and re-runs SOLGAS until it finds a quantity of that starting material for which the adiabatic temperature and threshold ignition temperature are equal. Specifics on the empirical threshold temperature are discussed below and in the main text of this report. FLAME4d is written in Borland, Inc.'s Turbo Pascal v 6.0, compiled for IBM PC compatible machines. It is a DOS program but generally is run in a DOS window under Windows 95.

FLAME4d is intended to use standard SOLGAS input files, specifically the format devised for the 1995 version 3.02b5 [16]. It will run SOLGAS via DOS redirection and the use of an internally generated macro file, read SOLGAS's output, alter the control macro, and re-run SOLGAS until the overall objective function converges to zero. The user creates a control file listing the runs desired and the variable that is to be altered during the boundary search (in this case, the initial quantity of any one of the starting materials). The program uses Newton's method to find the value satisfying the desired condition (namely, that the adiabatic temperature be equal to the empirical threshold temperature).

The algorithm used is as follows: initially, SOLGAS is run twice, the first time using quantities specified in the driver file for that run and the second time with the control variable slightly varied from its initial value. The results of these two runs are read by the driver program, and a new value for the control variable is interpolated or extrapolated from these results. This new value is used as the starting point for a second iteration, using the better of the previous two runs as the other starting point. As this process is repeated, the limits should converge to the desired value.

Twenty repetitions are allowed before the system gives up and goes to the next run in the series. This limit has proved adequate for the relatively smoothly varying systems treated so far. It is quite possible, however, for a particular run to have no meaningful solution (e.g., if one is in an "always non-flammable" region based on concentrations of nonvarying starting materials), and sometimes an attempt will fail because SOLGAS fails to solve an intermediate case presented to it in the course of the run. Failed cases do not get reported in the output file but do not halt the run.

The final reaction temperature supplied to SOLGAS is specified as being the empirical threshold temperature calculated for the current starting composition. Convergence is defined presently as "net reaction heat being within 0.02 kJ of zero." Typical overall heats of reaction for mixtures containing about 1 mole of starting material are on the order of 10 to 1000 kJ, so 0.02 allows at least three significant digit accuracy to the result (much more precise than the accuracy of the empirical correlation between flammability and adiabatic temperature). This value could be adjusted within the program but cannot be lowered a great deal without modifying SOLGAS as well (due to the number of significant digits reported for quantities and temperatures by SOLGAS).

To summarize, FLAME4d is set up to

(1) find the "net heat = 0" point.
(2) vary a single starting material's initial quantity.
(3) calculate a threshold ignition temperature from initial composition
(4) write a brief output file containing one line per final run, listing (run #, T, P, names and starting quantities of materials).

B.2.1 Files Used by FLAME4d

FLAME4d uses several files which are discussed below:

1. **FLAME4d.EXE** – the program itself.

2. **FLAME4d.prm** – a text file containing fit parameters for the empirical threshold temperature used to estimate flammability. These parameter values are separated from the compiled program to allow easy adjustment should additional experimental data create the need for recalibration or to allow use with other chemical systems. The best fit of publically available flammability

boundary data for fluorine and ClF_3 reacting with various PFCs and CFCs uses the parameter set shown in Exhibit B.3. A more conservative set, which adjusts the threshold downward to account for sparseness of experimental data and apparent system-to-system variability is shown in Exhibit B.4.

Exhibit B.3. File image of FLAME4D.PRM, showing "best fit" parameter values

```
Best fit  -- Boundary Parameter Set
rich 140.0 800
lean 110.0 1100
```

Exhibit B.4. File image of FLAME4D.PRM, showing "conservative fit" parameter values

```
Conservative fit -- Boundary Parameter Set
rich 85.0 900
lean 70.0 1050
```

The first line can be used as a title or description line. It is ignored by the program except that it will be repeated in the output file. The second line must begin with the word "rich" followed by the "A" and "B" parameter values defining the predicted rich-mixture adiabatic temperature threshold function. The next line must begin with the word "lean" and contain A and B values for the lean mixture temperature threshold function. The empirical formula for predicted adiabatic temperature is of the form

$$T_{lean} = A_{lean} / X_{oxidizer} + B_{leam}$$

and

$$T_{rich} = A_{rich} / S\ X_{fuel} + B_{rich}$$

where X is the mole fraction of the species in question and S is a stoichiometry parameter (supplied in a later data file), which specifically is the number of moles of oxidizer required to react the fuel to CF_4 (and to Cl_2 if chlorine is present in the fuel or oxidizer). These two temperatures are combined to yield the single temperature (predicted to be the necessary "ignition temperature" of the gas mixture) by a smoothing scheme:

$$T_{threshold} = (T^{-4}_{lean} + T^{-4}_{rich})^{-1/4}$$

The relationships given by these formula and parameter values are purely empirical.

3. **"Control" file** – a text file containing one line with system data, followed by any number of single lines describing each desired run. The first line of the file contains three numeric values. Each of these three numbers should be separated by one or more spaces. The first number is the

previously mentioned parameter S, the ideal stoichiometry for the fuel oxidizer combination under consideration. S is the number of moles of oxidizer required to completely react the fuel to CF_4 with no excess oxidizer, any Cl present in either fuel or oxidizer forming Cl_2. The second and third numbers are the indices of the oxidizer and the fuel, respectively. That is, if the oxidizer (say F_2) is the second starting material in the thermodynamics data file, the index used here is 2.

Each run description line consists of 4 to 8 numbers, each number separated by one or more spaces. The numbers, in order are:

Control variable – this designates the variable that will be adjusted by FLAME4d to zero in on the point at which the net heat is zero. A value of 1 or more indicates the starting material to be varied (in the order listed in this file).

Temperature (K) – Initial guess for reaction temperature, in K. This will be altered during the run and its initial value is not critical.

Pressure (bar) – the system will be run at this constant pressure.

Starting Amounts – Initial quantities of starting materials. The identity and order of the starting materials must be the same as that contained in the thermodynamics data file, whose name the user must supply when FLAME4d is run. Quantities are in moles.

An example of a control file is shown in Exhibit B.5.

Exhibit B.5. Sample control file for FLAME4d.EXE

```
2.0   2  3
2  1000  1.013    0      0.15  0.85
2  1000  1.013    0.085 0.15  0.765
3  1000  1.013    0.285 0.665 0.05
3  1000  1.013    0.38  0.57  0.05
```

The first line is the control line, which indicates that the ideal stoichiometry for this system requires 2 moles of oxidizer for 1 mole of fuel, that the oxidizer will be the second of the starting materials, and the fuel the third. In the next line, starting material 2 (the one listed as beginning with 0.15 moles) will be varied in an attempt to find a composition on the predicted flammability boundary, holding the other variables constant. The initial temperature used will be 1000 K (though this value will be adjusted and recalculated internally), and the system will be calculated at a pressure of 1.013 bar (i.e. 1 atm). Starting quantities will be 0, 0.15, and 0.85 moles for the three starting materials present in the SOLGAS data file. The second data set (defined by the third line in the file) varies the initial starting material quantities. In the third mixture (the fourth line in the file), starting material number 3 will be varied instead of material

2. Note that the spacing of the entries is not important as long as at least one space separates each entry. The total length of a single line, however, should not exceed 80 characters. The name of this file will be requested by FLAME4d, and a path may be specified.

4. & 5. **Temporary files** – Two temporary files are used. These are named $$temp.mac and $$temp.out. The first is a macro which contains the keystrokes that SOLGAS needs to run each point. The second is the output of a SOLGAS run. These files are repeatedly created and deleted as the run progresses. They needn't be provided by the user but may appear temporarily in directory listings during running of the program (do not delete them while the program is operating!). They may remain if the program or computer crashes during a run, or is manually halted.

6. **SOLGAS** – As presently configured, FLAME4d is designed to use SOL302b5.EXE, but this must be named SOLGAS.EXE. It must be in the same directory as FLAME4d.EXE.

7. **Thermodynamics Data file** – When SOLGAS is run, it requires a file containing thermodynamic data for the species of interest. The structure of this file is described in ref 16, but sample files for most systems of interest have been created and should be present with the program FLAME4d. At least two species must be designated as starting materials, one a fuel and one an oxidizer. Normally, one or more diluents will also be specified. SOLGAS will calculate equilibria for systems with more than one initial fuel or oxidizer, but the program FLAME4d, dependent as it is on the stoichiometry parameter "S" will not directly take into account more than one fuel and oxidizer, and thus will not (as presently constituted) gracefully handle multiple reactants. The user is asked for the name of this file when FLAME4d is run, and may specify a path. A sample of such a file was shown in Exhibit B.1.

8. **Results file** – FLAME4d writes its results to an ASCII file in a format that can be directly imported into most spreadsheets, generally termed "quote and comma delimited text" format; Microsoft terms such files "comma separated variable" files. Lotus and Quattro specifically look for filenames with the extension ".PRN" when importing such files.

As presently configured, the FLAME4d results files contain a header line, then a series of lines for each case run. Each such line contains

Run No., Temperature, Pressure, Volume, Heat, many (Starting material entries),

where each (Starting material entry) consists of a "name" and "starting quantity." A name for the results file will be requested when FLAME4d is run, and a path may be specified.

B.2.2 Operation of FLAME4d

1. Assemble the data files you need to run SOLGAS and FLAME4d. These are

   a. SOLGAS.EXE
   b. FLAME4d.EXE
   c. FLAME4d.prm
   d. Thermodynamic data file
   e. Control file

2. From Windows, run the file FLAME4d.EXE (e.g., by double clicking its icon). It should open and run in a DOS window.

3. Answer the queries about the three file names, namely the "SOLGAS thermodynamics data file name," "Control file name," and "Results file name".

FLAME4d will now run through the list of points designated in the control file. While running, it will display a status line telling which run it is on and a few control variables to give the user an idea of how things are progressing. When done with all runs, it will type "Finished" and terminate. A display of a message "failed to converge" during this display indicates that a solution could not be found. No output will be created in such cases for that particular run.

APPENDIX C

THERMODYNAMICS DATA USED IN THE MODELS

Thermodynamics data used in the detonation theory models are listed in Table C.1. ΔH_f^o values are from the JANAF thermochemical tables [13] where available or, in a few cases, from other sources referenced in the thermodynamics library associated with [16]. Heat capacity parameters fit tabular data to the function.

$$C_P(T) = a + b/T + c/T^2 + d/T^3 + e/T^4$$

The parameter values are either from the original 1992 explosion theory models or are refit from tabular data (where available). In all cases the fit is reasonably good over the temperature range 300 to 4000 K. As described in the main body of the report, a few species, for which no high temperature C_P data were available, had parameters adjusted to match a statistical mechanically limiting value at high temperature. Following the original spreadsheet model, the energy units used are (gm)-calories.

Table C.1. Thermodynamic parameters used in detonation pressure models

Gas	ΔH_f^o	C_P coefficients (cal/mol K)				
	cal/mol	a	b	c	d	e
N_2	0	9.505	-2105.23	417418	2.883E+07	-9.703E+09
O_2	0	10.803	-4231.87	2152124	-5.225E+08	4.612E+10
F_2	0	10.249	-2289.79	1172917	-3.276E+08	3.189E+10
Cl_2	0	10.074	-2304.06	1529839	-4.501E+08	4.327E+10
$CFCl_3$	-69000	26.088	215.86	-3267204	9.210E+08	-7.844E+10
HF	-65140	10.116	-5414.18	3272949	-8.187E+08	7.147E+10
HCl	-22302	9.987	-3822.51	1739084	-3.382E+08	2.381E+10
ClF	-12020	9.598	-1120.78	474919	-1.401E+08	1.377E+10
ClF_3	-37970	19.852	114.89	-794889	1.228E+08	-5.306E+09
ClO_2F	-6040	17.443	3957.71	-3847539	9.561E+08	-7.884E+10
ClO_3F	-4876	25.821	181.67	-2830380	7.716E+08	-6.455E+10
CF_3CF_2Cl	-261500	41.183	5895.18	-10300102	3.585E+09	-4.346E+11
CO_2	-94054	15.876	-2921.18	-140251	1.921E+08	-2.248E+10
CF_4	-223040	25.818	215.86	-3267204	9.210E+08	-7.844E+10
COF_2	-152700	20.005	-578.30	-2288030	7.256E+08	-6.611E+10
CF_2ClCF_2Cl	-212811	41.978	6310.22	-11085975	4.029E+09	-4.873E+11
CF_3Cl	-169200	25.918	215.86	-3267204	9.210E+08	-7.844E+10
CF_2Cl_2	-117500	26.018	215.86	-3267204	9.210E+08	-7.844E+10
UF_6	-513441	37.729	113.09	-1010202	1.076E+08	1.448E+09
H_2O	-57798	15.776	-8142.84	1864910	5.132E+08	-1.647E+11
C_2F_2	5000	20.832	285.90	-3154180	1.240E+09	-1.541E+11
C_2F_4	-157400	31.733	504.49	-5000076	1.837E+09	-2.156E+11
C_2F_6	-321200	42.667	438.27	-4109917	8.262E+08	-2.862E+10
n-C_3F_8	-406000	56.663	17915.44	-30922505	1.251E+10	-1.683E+12
c-C_4F_8	-352000	74.640	-34634.70	48098980	-2.677E+10	4.339E+12
n-C_4F_{10}	-511472	80.227	-4003.65	5760480	-6.165E+09	1.176E+12
SiF_4	-385980	25.786	318.95	-2166332	5.410E+08	-4.216E+10

Thermodynamics data for species used with SOLGAS in calibration or use of the equilibrium-based flammability limit model are taken from the data library associated with ref. [16]. most of which derive from ref. [13]. Data values used are listed in Exhibit B.1 in Appendix B. In that table, for each species listed the thermodynamic values for dHf (i.e:, $\Delta H_f^o(298.15K)$), S (i.e., $S^o(298.15K)$) and parameters a, b, c, d, and e for C_P are listed. These last parameters are for the temperature function used by SOLGAS, namely:

$$C_P = a + b\,T + c\,T^2 + d\,/\,T^2 + e\,/\,T^3$$

All values are for the reference temperature of 298.15 K and energy units in this data set are measured in joules.

APPENDIX D

CALIBRATION OF FLAME LIMIT CORRELATIONS

D.1. EXPERIMENTAL DATA USED IN CALIBRATIONS

As indicated in the text, the prediction methods discussed in this report are based on empirical correlation between computed post-reaction temperatures and experimental information on ignitability of gas mixtures. Each prediction method developed a threshold temperature which is a function of flammable gas composition. Both methods need to be calibrated to available experimental data. The data used for this purpose are listed in this appendix.

Data points were taken from experimental work derived from several sources. Some of those experiments were explicitly designed to find flammability boundaries, while others more or less incidentally determined such boundaries in the course of investigating flame behavior well within the boundary of compositions which could sustain a flame. The experimental data used consist of the composition of mixtures which would (or would not) burn. Initial temperature and pressure can have some influence on flammability, and, where stated, it was recorded, although all initial conditions were near 1 atmosphere and room temperature.

The experimental initial conditions (temperature, pressure, and composition) were provided as inputs to the appropriate detonation theory model and to ADIAB95/SOLGAS. From these, the isentropic (i.e., constant volume adiabatic) temperature T_{iso} in the first case, or the constant pressure adiabatic temperature T_{ad} in the second, were computed . These compositions and computed temperatures are listed in Table D.1. There is frequently a large difference between the two computed temperatures. This is due primarily to the inclusion of radicals and other low-temperature unstable species as possible products in the equilibrium model, with a lesser contribution from the fact that constant volume adiabatic temperatures will generally be somewhat higher than constant pressure adiabatic temperatures in reactions such as these.

D.2 FLAMMABILITY CORRELATION USED IN DETONATION MODELS

The threshold function used in Barber's 1992 predictions, and which is retained here in the detonation model spreadsheets is:

$$T_{threshold} = A \ \ln (X_{oxidizer}/X_{fuel}) + B \quad ,$$

the empirical flammability criterion being that if $T_{iso} > T_{threshold}$, the mixture is predicted to be flammable. Figure D.1 plots T_{iso} versus the function $(X_{oxidizer}/X_{fuel})$ on a semilog plot for all flame boundary data points in the six systems for which spreadsheets were constructed.

Table D.1. Experimental data used in calibration of flame limit correlations[a]

P(bar)	Xi(dil)	Xi(Ox)	Xi(Fu)	Key	System	T_{iso}(K)	T_{ad}(K)	S
1.013	0	0.89	0.11	b?	L318(64)	2669	1370	2.667
1.013	0	0.55	0.45	b?	L318(64)	2542	1934	2.667
1.013	0	0.577	0.423	w	L218	NA	2353	1.333
1.013	0	0.55	0.45	w	L218	NA	2301	1.333
1.013	0	0.63	0.37	w	L218	NA	2126	1.333
1.013	0	0.564	0.436	w	L218	NA	2340	1.333
1.013	0	0.417	0.583	w	L218	NA	1767	1.333
1.013	0	0.377	0.623	w	L218	NA	1620	1.333
1.013	0	0.458	0.542	w	L218	NA	1912	1.333
1.013	0	0.485	0.515	w	L218	NA	2012	1.333
1.013	0	0.512	0.488	w	L218	NA	2129	1.333
1.013	0	0.592	0.408	w	L218	NA	2328	1.333
1.013	0	0.525	0.475	w	L218	NA	2191	1.333
1.013	0	0.499	0.501	w	L218	NA	2070	1.333
1.013	0	0.351	0.649	b+	L218(64)	NA	1523	1.333
1.013	0	0.656	0.344	b -	L218(64)	NA	2016	1.333
1.013	0	0.4	0.6	w	L218	NA	1705	1.333
1.013	0	0.456	0.544	w	L218	NA	1905	1.333
1.013	0	0.511	0.489	w	L218	NA	2124	1.333
1.013	0	0.553	0.447	w	L218	NA	2311	1.333
1.013	0	0.608	0.392	w	L218	NA	2245	1.333
1.013	0	0.738	0.262	n/b	L218(64)	NA	1705	1.333
1.013	0	0.456	0.544	b-	L116	NA	1881	0.667
1.013	0	0.422	0.578	w	L116	NA	1973	0.667
1.013	0	0.387	0.613	w	L116	NA	1996	0.667
1.013	0	0.375	0.625	w	L116	NA	1950	0.667
1.013	0	0.369	0.631	w	L116	NA	1927	0.667
1.013	0	0.367	0.633	w	L116	NA	1919	0.667
1.013	0	0.365	0.635	w	L116	NA	1912	0.667
1.013	0	0.36	0.64	w	L116	NA	1893	0.667
1.013	0	0.345	0.655	w	L116	NA	1837	0.667
1.013	0	0.303	0.697	b+	L116	NA	1663	0.667

Table D.1, continued

P(bar)	Xi(dil)	Xi(Ox)	Xi(Fu)	Key	System	T_{iso}(K)	T_{ad}(K)	S
0.8	0	0.8	0.2	w	F318	6193	2778	4
0.8	0	0.667	0.333	w	F318	4041	2514	4
0.8	0	0.571	0.429	w	F318	3009	1805	4
0.8	0	0.5	0.5	w	F318	2468	1569	4
0.8	0	0.421	0.579	w	F318	1978	1287	4
0.8	0	0.333	0.667	w	F318	1531	1016	4
0.8	0	0.308	0.692	w	F318	1416	965	4
0.8	0	0.286	0.714	w	F318	1322	926	4
0.8	0	0.235	0.765	b	F318(83)	1121	836	4
0.8	0	0.229	0.771	b	F318(83)	1096	823	4
1.013	0	0.930	0.070	b	F318(68)	3745	1546	4
1.013	0	0.924	0.076	bx	F318(68)	3938	1710	4
0.8	0	0.910	0.090	w	F318	4321	2302	4
0.8	0	0.885	0.115	w	F318	4882	2721	4
0.8	0	0.88	0.12	w	F318	4983	2737	4
0.8	0	0.86	0.14	w	F318	5350	2771	4
0.8	0	0.73	0.27	w	F318	4878	2710	4
0.8	0	0.6	0.4	w	F318	3273	1928	4
0.8	0	0.49	0.51	w	F318	2400	1536	4
0.8	0	0.421	0.579	w	F318	1978	1287	4
0.8	0	0.41	0.59	w	F318	1917	1246	4
0.8	0	0.38	0.62	w	F318	1758	1142	4
0.8	0	0.32	0.68	w	F318	1470	989	4
1.013	0	0.38	0.62	bx	F318(68)	1758	1150	4
0.8	0	0.667	0.333	w	F218	NA	1833	2
0.8	0	0.5	0.5	w	F218	NA	1477	2
0.8	0	0.408	0.592	w	F218	NA	1393	2
0.8	0	0.385	0.615	w	F218	NA	1273	2
0.8	0	0.351	0.649	w	F218	NA	1213	2
0.8	0	0.333	0.667	w	F218	NA	1081	2
0.8	0	0.286	0.714	w	F218	NA	1040	2
0.8	0	0.267	0.733	w	F218	NA	1004	2
0.8	0	0.247	0.753	b?	F218(83)	NA	965	2
0.8	0	0.222	0.778	n/b	F218	NA	982	2

Table D.1, continued

P(bar)	Xi(dil)	Xi(Ox)	Xi(Fu)	Key	System	T_{iso}(K)	T_{ad}(K)	S
0.8	0	0.417	0.583	w	F116	NA	2003	1
0.8	0	0.385	0.615	w	F116	NA	1745	1
0.8	0	0.323	0.677	w	F116	NA	1453	1
0.8	0	0.286	0.714	w	F116	NA	1294	1
0.8	0	0.25	0.75	b?	F116(83)	NA	1152	1
0.8	0	0.2	0.8	n/b?	F116	NA	1002	1
1.013	0	0.175	0.825	b	F114	1109	954	2
1.013	0.2	0.16	0.64	b	F114	1190	995	2
1.013	0.4	0.14	0.46	b	F114	1280	1053	2
1.013	0.55	0.12	0.33	b	F114	1343	1105	2
1.013	0.7	0.114	0.186	b	F114	1628	1358	2
1.013	0.75	0.11	0.14	b	F114	1746	1453	2
1.013	0.77	0.11	0.12	b	F114	1830	1507	2
1.013	0.79	0.125	0.085	b	F114	1938	1668	2
1.013	0.76	0.17	0.07	b	F114	2239	1808	2
1.013	0.75	0.19	0.06	b	F114	2306	1703	2
1.013	0.7	0.24	0.06	b	F114	2296	1645	2
1.013	0.55	0.38	0.07	b	F114	2485	1522	2
1.013	0.4	0.53	0.07	b	F114	2454	1331	2
1.013	0.2	0.72	0.08	b	F114	2614	1312	2
1.013	0	0.92	0.08	b	F114	2574	1264	2

Key: **b** = on flammability boundary; **n/b** = does not burn; **b** + or **b** - = upper or lower flammability limit; **w** = well within flammability boundary; **x** = detonates

P is the initial pressure in bar;

T_{iso} is the isentropic temperature calculated in the appropriate detonation model spreadsheet for this composition;

T_{ad} is the adiabatic temperature calculated for this composition by ADIAB95/SOLGAS;

S is the stoichiometry ratio used in the equilibrium-based model correlation.

System: chemical system and data source

code	system	reference
L318	$ClF_3 + c\text{-}C_4F_8$	[6]
L218	$ClF_3 + C_3F_8$	[6]
L116	$ClF_3 + C_2F_6$	[6]
F318	$F_2 + c\text{-}C_4F_8$	[8] (83) or [7] (68)
F218	$F_2 + C_3F_8$	[8] (83) or [7] (68)
F116	$F_2 + C_2F_6$	[8] (83) or [7] (68)
F114	$F_2 + C_2F_4Cl_2$	[2] and [3]

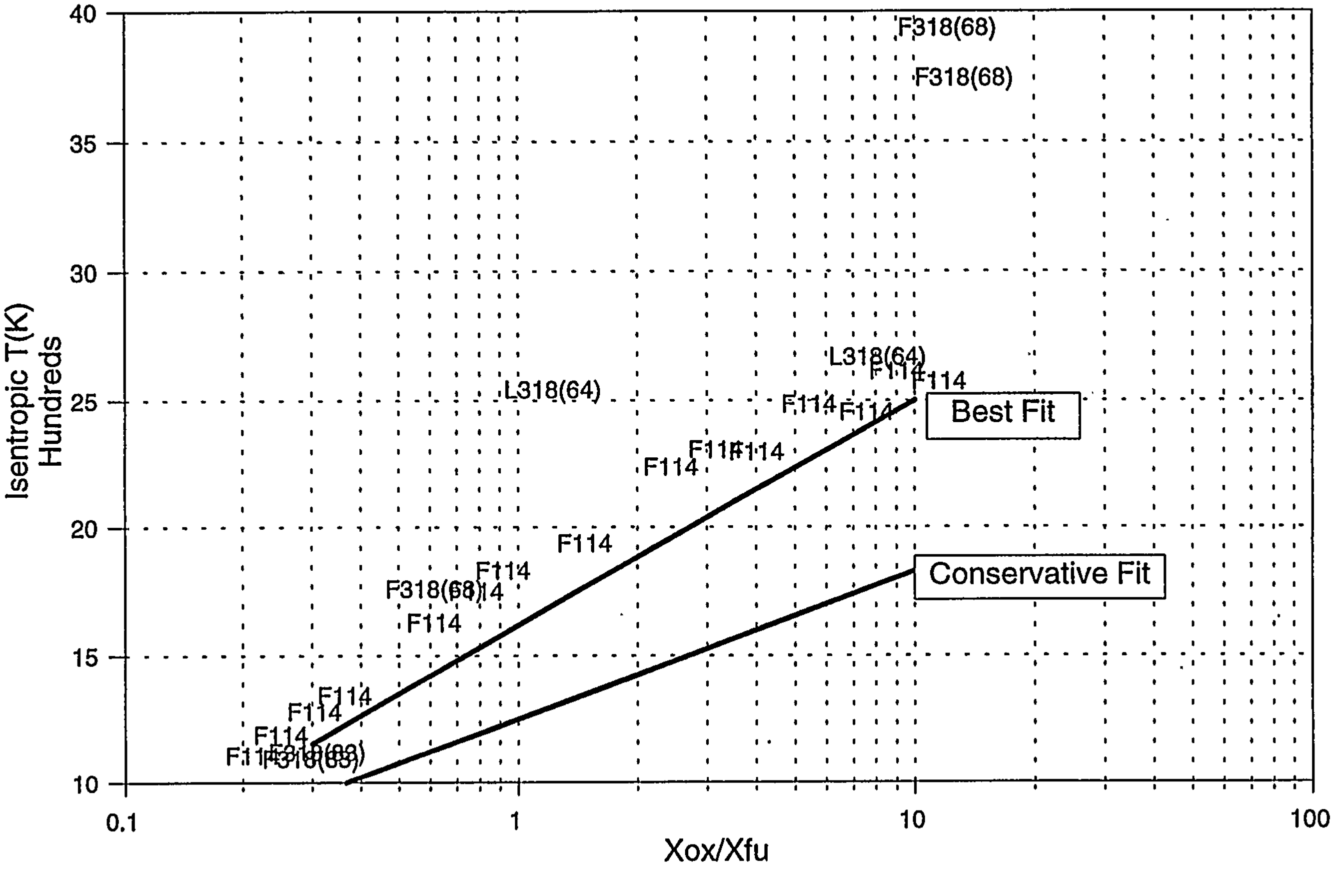


Figure D.1 Correlation boundaries and isentropic temperature computed by detonation theory models for mixtures experimentally known to be on flammability boundaries (see text and Table D-1 for definitions of data codes).

Two boundaries are drawn which divide the region of the graph containing boundary points from a region not containing such points. The one labeled "best fit" is the line drawn closest to the lowest temperature boundary points. It is evident from inspection of the graph, however, that there is considerable system-to-system and inter-system variability in the points (when plotted using these functions). It is likely that were data available for additional systems, the variability would persist, and some data points would fall below the "best fit" line. Since the prediction scheme used claims that any composition whose isentropic temperature falls below the line is not flammable, that would mean that the correlation would predict that some mixtures are non-flammable which, in fact, might prove to be flammable. In an attempt to allow for this variation, a second correlation line is drawn which attempts to capture and allow for a certain degree of variability in this (imperfect) correlation. That line is labeled "conservative fit" in Figure D.1. The parameters for these two lines are as follows::

"Best fit":	$A = 383$,	$B = 1617$
"Conservative fit":	$A = 250$,	$B = 1251$

D.3 EQUILIBRIUM BASED CORRELATION

Among various correlation functions examined for use in the equilibrium-based flammability limit model, the function chosen was a two-part function, with a threshold temperature function fit for lean and rich mixtures. The function for lean mixtures is:

$$T_{lean} = A_{lean} / X_{oxidizer} + B_{lean} \quad ,$$

and for rich mixtures,

$$T_{rich} = A_{rich} / (S\, X_{fuel}) + B_{rich} \quad .$$

The two threshold temperatures are combined smoothly by the function

$$T_{threshold} = (T_{lean}^{-4} + T_{rich}^{-4})^{-1/4} \quad .$$

As before, experimental compositions known to burn are plotted in the form appropriate to the correlation equations used. In this case, the data points are separated into "lean" (excess oxidizer) and "rich" (excess fuel) sets and plotted separately. Fig. D.2 plots the adiabatic temperature for lean mixtures vs $1/X_{oxidizer}$ and Fig. D.3 plots adiabatic temperatures for rich mixtures vs $1/ S\, X_{fuel}$, where S is the ideal stoichiometry ratio, the number of moles of oxidizer needed to completely react the fuel to CF_4 (and Cl_2, if applicable). As before, two correlation lines are drawn in each plot, one the closest line to the available data that could be drawn and still encompass all flammable compositions, and the other ("conservative") correlation which moves the line away from the flammable region to account for data variability. The resulting

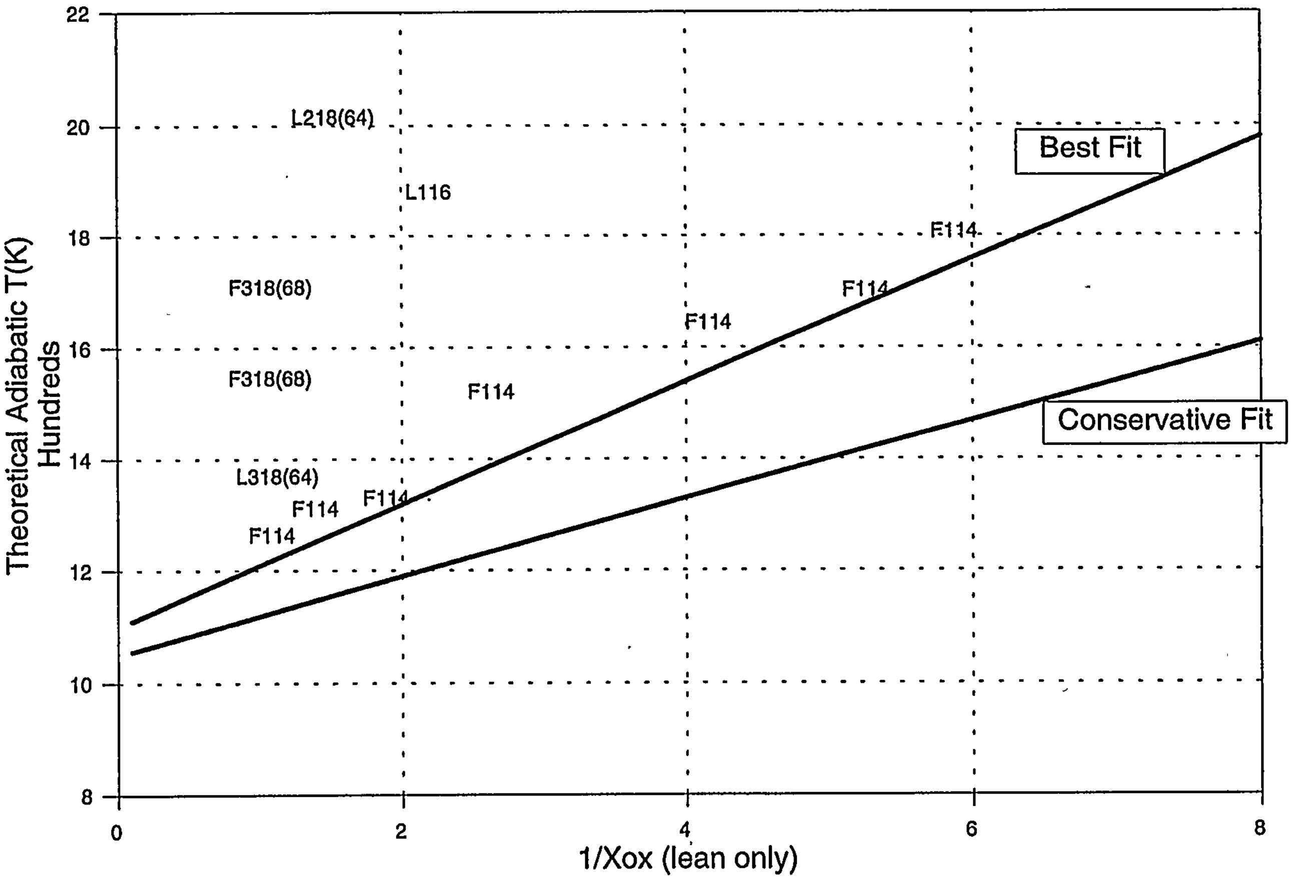


Figure D.2 Correlation boundaries and adiabatic temperature computed for mixtures experimentally known to be on flammability boundaries (see text and Table D-1 for definitions of data codes).

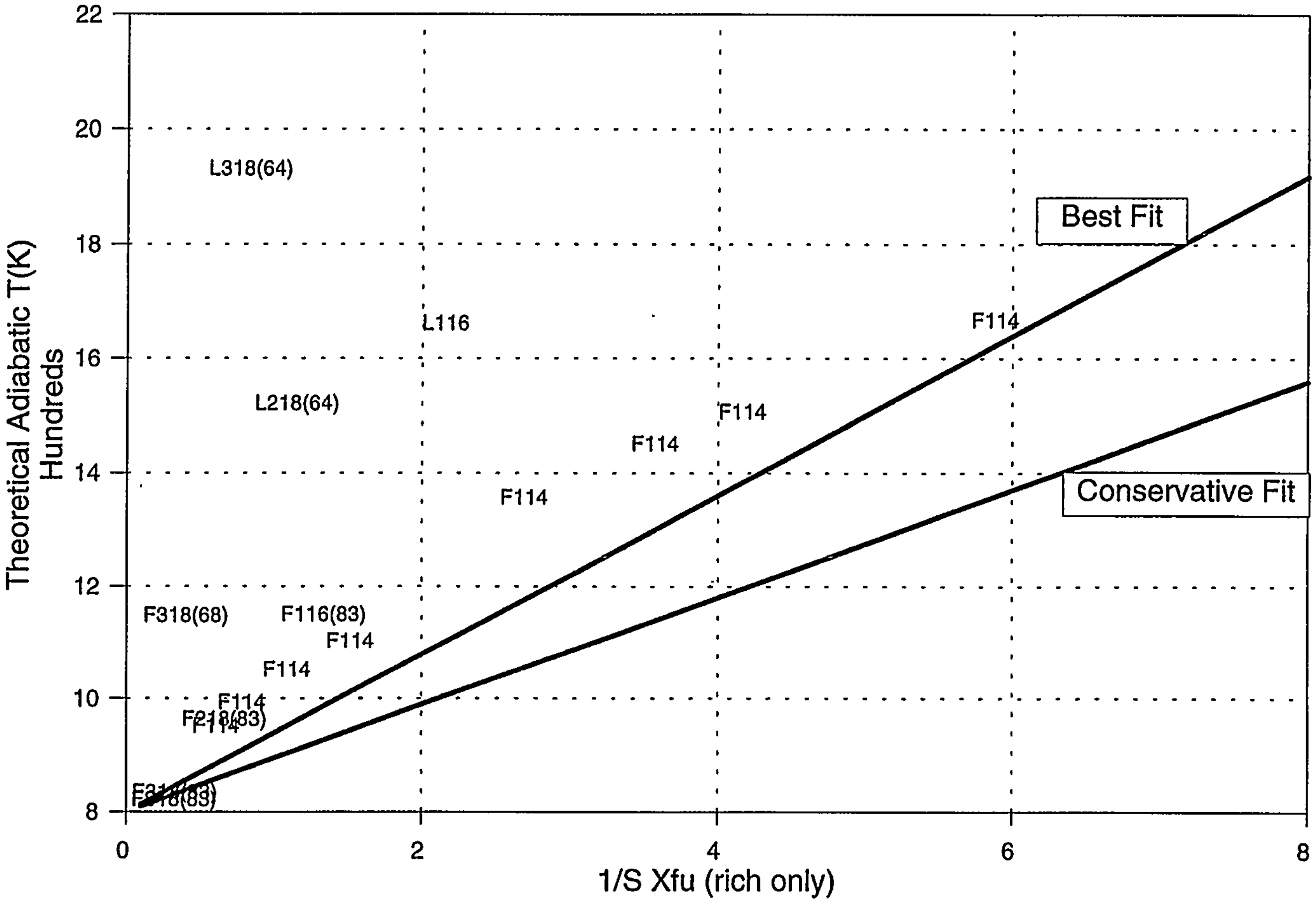


Figure D.3 Correlation boundaries and adiabatic temperature computed for mixtures experimentally known to be on flammability boundaries (see text and Table D-1 for definitions of data codes).

parameter values are:

Best Fit	Lean	A = 110 ;	B = 1100
	Rich	A = 140 ;	B = 800
Conservative Fit	Lean	A = 70 ;	B = 1050
	Rich	A = 95 ;	B = 800

D.4 NOTES ON EXPERIMENTAL FLAMMABILITY LIMIT DATA

Flammability limits obtained from literature data were from several sources. Fletcher and Ambs [6] examined combustion of binary mixtures of ClF_3 with C_2F_6, C_3F_8, and c-C_4F_8. They suggested that the ignition temperature. for such mixtures might be fairly low and similar for all fluorocarbons but did not propose a value for that temperature. This work was mainly a study of flame speeds and quench distances, rather than composition boundaries, but as compositions were varied, some information was obtained relevant to the current study. For ClF_3 + C_2F_6, at the lower flammability limit, 54.4% fuel didn't burn, while 57.8% did; at the upper limit, 69.7% was the highest mixture that burned. For the C_3F_8 mixtures, the lower limit lies between 26.2% (not ignitable) and 34.4% (ignitable) and the upper limit lies at 64.9% ± 0.1% fuel. Data on c-C_4F_8 was of poorer quality, as the mixtures had a tendency to detonate. From the limited data, a rough estimate of the flammable composition range is 11% to 45% c-C_4F_8. Unfortunately, there was no mention in the article of the initial pressure and temperature of the gas mixtures. In using the boundary limit information, we assume standard conditions (1 atm, 25°C).

Fletcher and Kittelson [7] studied detonation limits of F_2 + c-C_4F_8 mixtures, observing detonation velocities between 1000 and 1600 m/s over compositions ranging from 62% down to 7.62% fuel. (Incidentally, these detonation velocities are in approximate agreement with those predicted in the spreadsheet models discussed in this report). Flame boundaries were not explicitly studied and are likely to lie a bit outside the composition envelope which can generate a detonation. One run was reported in which a 6.08% fuel mixture burned. Again, the initial pressure and temperatures were not reported in this study.

Fletcher and Hinderman examined the combustion of rich mixtures of F_2 and one or more of C_2F_6, C_3F_8, and c-C_4F_8 . These studies concentrated primarily on product composition and did not explicitly seek the upper flammability limit. Gas mixtures at room temperature and 600 Torr were ignited by spark and products analyzed by gas chromatography. An approximate upper flammability boundary can be obtained by examination of graphs showing the compositions at which formation of reaction products ceases. For C_2F_6:, this level was 75 % fuel; for C_3F_8 , it was 75.3 % fuel; for c-C_4F_8, a 76% fuel mixture burned, but no higher fuel concentration results were displayed, so the boundary presumably lies somewhat higher than this.

Bernhardt et al. explicitly studied flammability boundaries for F_2 /CFC-114/N_2 and also for other systems (fuel = CFC-114a, $C_6F_{10}(CF_3)_2$, and $C_4F_7Cl_3$) [2][3]. Initial conditions were at 1 atm and 107°C. This work was taken from reference [4], which contains information on additional systems. As that reference remains classified at present, no information from it was used in preparation of this report. The boundaries for CFC-114a are, to the accuracy of the models under consideration here, identical to that for CFC-114. The other two fuels were not considered as candidates for calibration for the models due to lack of thermodynamic data for those compounds.

Bauer and Hamilton [5] published study of the flammability limits of F_2 / N_2 mixtures using as fuels C_4F_{10}, CFC-114, and other similar compounds not of direct interest to this work. That study, however, was published as proprietary to 3M, and the information was not used in this work.

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