Modeling of N₂O Decomposition Events

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Abstract

This paper addresses the safety issues associated with the oxidizer nitrous oxide (N₂O) with emphasis on propulsion systems. Even though N₂O is a widely used energetic material, the number of decomposition related accidents are quite limited due to its abnormally slow decomposition kinetics. However hazards do exist especially in propulsion systems where large quantities of N₂O are stored at room temperature in thin walled vessels. Moreover the closely coupled combustion chamber is a significant source for ignition which does not naturally exist in other applications. A detailed kinetics model for the N₂O decomposition process is presented. It is shown that a simplified single step first order kinetics model accurately captures the decomposition process at pressures larger than 40 atm. With use of the kinetics data, it has been shown that, at the same pressure and temperature, the N₂O decomposition rate is six orders of magnitude slower than the decomposition of hydrogen peroxide (H₂O₂), making it a much safer propellant. Models for homogenous and local thermal ignition are also presented. It is shown that the estimated minimum ignition energy for pure N₂O is approximately 450 mJ which is three orders of magnitude larger than the ignition energy for a stoichiometric CH₄/air mixture. Small concentrations of diluents (i.e. N₂, O₂ or He) further increase the ignition energy making the mixture extremely difficult to ignite at dilution levels higher than 30%. The results of a model developed to predict the pressure rise in a closed vessel subject to decomposition is presented to demonstrate the significant hazard that exists in the N₂O tank. The model predicts a 20 fold increase in pressure over a time period of many seconds for tanks that are in the range of 1-3 meters in length. Finally, a list of safety related recommendations unique to N₂O operations have been included. The general conclusion is that despite its potential decomposition hazard, if handled properly, N₂O is one of the safest oxidizers being used in rocket propulsion systems.

I) Nomenclature

A :	Surface area of the vessel
A_r :	Reaction rate coefficient
C_i :	Non-dimensional molar concentration of the ith species
C_{pf} :	Specific heat of the products at constant pressure
$\overline{C}_p$:	Average specific heat at constant pressure across the flame
$\hat{c}_v$:	Average molar heat capacity of the gas mixture

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$\hat{c}_{vo}$:	Specific heat of the unburned mixture
D:	Hydraulic diameter of the vessel
E_a :	Activation energy
E_H :	Non-dimensional energy parameter
f_{N2} , f_{O2} :	Initial molar concentrations of N_2 and O_2 in the mixture
h:	Convective heat transfer coefficient
$[I]$:	Molar concentration of the Ith species
k_i :	Reaction constant for the ith elementary reaction
k_1^∞ :	High pressure rate constant
$\bar{k}_1^\infty$:	High pressure rate constant for H_2O_2
k_1^o :	Low pressure rate constant
L:	Length of the vessel
M:	Collision partner
m :	Stoichiometry of the reaction
Nu :	Nussel number
n_p :	Total moles of products
n_r :	Total moles of reactants
P_{max} :	Maximum pressure in the vessel
P_o :	Initial pressure of the system
R_u :	Universal gas constant
s:	Entropy
S_L :	Laminar flame speed
T , $\bar{T}$:	Temperature and non-dimensional temperature
T_a :	Activation temperature
T_f :	Adiabatic flame temperature at constant pressure
T_{fave} :	Average temperature in the tank at the end of the decomposition process
T_M :	Overheating limit
T_o :	Initial N_2O vapor temperature
T_w :	Wall temperature of the vessel
t , $\bar{t}$:	Time and non-dimensional time
V:	Volume of the vessel
x_{N2O} :	Initial mole fraction of nitrous oxide
z_{N2O} :	Compressibility of N_2O
$\Delta \hat{H}_G$:	Molar heat of reaction of the global reaction
$\Delta \hat{H}$:	Molar heat of reaction of the elementary reaction
λ :	Coefficient of thermal conduction for the gas mixture
λ_f :	Coefficient of thermal conduction for the decomposition products
ρ_o :	Density of the unburned vapor or vapor/gas mixture
τ_c :	Cooling time scale
τ_d :	Characteristic time for decomposition
τ_r :	Reaction time scale

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II) Introduction

Nitrous oxide and liquid oxygen are the most commonly used oxidizers in hybrid rocket systems. This is primarily due to their cost, safety, availability and handling advantages compared to the other liquid oxidizers that can be used in propulsion applications. Despite its moderate Isp performance and poor impulse density at room temperature, N_2O has been the choice for small motors for which the systems and operational simplicity are the dominant driving forces. This fact explains the extensive use of N_2O in amateur rocketry and in many sounding rocket programs. Two good examples of N_2O based hybrid sounding rockets are the Hyperion system[1] which has been designed and flown by a private company, eAc, under the HPDP program and the currently ongoing NASA/Stanford Peregrine[2] effort.

The most impressive demonstration of a N_2O hybrid to date is the X-Prize winning SpaceShipOne system. The larger follow on SpaceShipTwo vehicle, which is designed to carry tourists into space on a sub-orbital flight, is also baselined for a N_2O hybrid propulsion system. If successful, this will be the first operational large scale hybrid rocket in commercial or military use. Unfortunately, the recent fatal accident at the Mojave Airport during a cold flow test of the SpaceShipTwo propulsion system has raised some safety concerns with the use of N_2O as an oxidizer. The primary hazard associated with N_2O is related to its energetic nature, namely its release of thermal energy by molecular decomposition. Although this exothermic behavior presents significant benefits in terms of the theoretical Isp performance and motor stability/efficiency characteristics, it also introduces a chemical explosion hazard in the various components of the rocket system including the oxidizer tank and the feed lines. Even though the hazard itself has been known well before the Scaled accident, the understanding of the decomposition process in practical systems has been lacking. The deficiency in the understanding, modeling and testing of the decomposition chemistry of N_2O is highly problematic, since it introduces unknown risks in the development of large scale N_2O propulsion systems.

There have been a limited number of studies reported in the open literature of which two are worth noting. The earlier effort[3], which was funded by the Air Force, has concentrated on establishing the explosion boundaries for pure N_2O and a few N_2O/diluent mixtures. Tests were conducted in a 1.5 inch diameter vessel made out of stainless steel. The ignition was initiated by copper and platinum wires which were heated electrically. Both slow reactions and explosions have been observed during testing. No attempt was made to measure the ignition energy. Unfortunately both wire materials used to ignite nitrous oxide are highly catalytic with N_2O, especially at elevated temperatures, compromising the usefulness of the data presented in the report.

The second study[4], which was also supported by the Air Force, is a more comprehensive effort that covers decomposition tests conducted in pipes with diameters, 1/2 in, 1 in, 2 in and 6 in. Pure N_2O in both vapor and liquid phases and also N_2O diluted with helium have been included in the testing. The ignition energies were not measured precisely, but some rough, possibly unreliable, estimates were included in the report. Unfortunately most of the testing with pure N_2O was at pressures lower than 40 atm, limiting the application of the data to propulsion systems. Two important findings from this study that are worth noting are 1) it was not possible to ignite N_2O in the liquid phase even with the use of blasting caps and 2) even at low concentrations helium as a diluent was quite effective in increasing the ignition energy. Both of these observations are consistent with SPG's experience base and also with the other studies reported in the open literature.

Even though these two reports contain useful data, neither of them present an understanding based on a theoretical framework which is critical in establishing the scaling laws needed in the design and testing of scale up systems. In this paper, our primary objective is to evaluate and assess the hazards that exist in N_2O based propulsion systems by using the fundamental understanding of the N_2O decomposition physics/chemistry. A Second goal is to establish a list of practical recommendations for the safe use of nitrous oxide.

Descriptive sections on the general properties and applications of N_2O, reported N_2O decomposition accidents and hazards unique to propulsion system have been included in order to give the reader a broader insight on this interesting material. The descriptive sections are followed by discussions on the fundamental

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aspects of the N_2O decomposition process, including the decomposition physics of the molecule and the chemical kinetics mechanisms that govern the decomposition chemistry. A direct comparison between N_2O and other energetic materials used in rocket propulsion (i.e. H_2O_2) is also included to demonstrate the relative safety of N_2O. The section on the homogenous and local ignition is followed by a brief discussion on N_2O decomposition explosions in closed vessels such as oxidizer tanks. A list of recommendations is also included in the final section of this paper.

III) General Properties and Applications of Nitrous Oxide

Nitrous oxide is a widely used substance with very interesting physical, chemical and biological properties. The general characteristics of N_2O, some of which are relevant to propulsion system applications, are discussed in the following paragraphs. Selected material properties and molecular constants for N_2O are listed in Table 1[5].

Table 1: Selected material properties and molecular constants for N_2O.

Material Property	
Melting Point	-90.86 C
Normal Boiling Point	-88.48 C
Critical Temperature	36.5 C
Critical Pressure	71.7 atm
Critical Density	0.452 g/cm^3
Heat of Fusion	1.563 kcal/mol (-90.86 C)
Heat of Vaporization	3.956 kcal/mol (-88.48 C)
Enthalpy of Formation	19.61 kcal/mol (25 C)
Dielectric Constant	2.023 (70 K)
Molecular Constants	
Dipole Moment	0.166 D
Fundamental Vibration Frequencies	1276.5, 589.2, 222.7 cm^{-1}

A) Physical Properties

Nitrous oxide is a colorless gas at standard temperature and pressure (STP) with a slightly sweet odor. It has a vapor pressure of 55.5 atm (816 psia) at 25C. The high vapor pressure of nitrous oxide at room temperature allows for self pressurization, making N_2O an ideal propellant for small propulsion systems for which the simplicity advantage dominates the Isp performance disadvantage of this relatively low energy oxidizer. For the sake of completeness, a brief description of the phase behavior of nitrous oxide is included in the Appendix.

The fact that nitrous oxide operates on its saturation dome (for blow down systems) or slightly above it (for supercharged systems), requires complicated two phase flow modeling in the feed system including the injector elements. The commonly observed low discharge coefficient of the injector orifices is a result of the two phase flow complications associated with the use of this flashing liquid.

It is widely accepted that nitrous oxide is a highly effective global anthropogenic green house gas which is 300 times more effective than carbon dioxide in trapping heat (its Global Warming Potential, GWP, is 310 in a 100 year time horizon)[6]. The higher effectiveness of nitrous oxide is due to its extremely long lifetime in the atmosphere. Recently, a significant amount of research effort has been devoted to developing methods to control the production rate of Nitrous Oxide in various industrial processes. The most significant human based release of N_2O is due to the production of nitric and adipic acids, land cultivation/fertilizers and emissions generated by biomass and fossil fuel combustion[7]. The level of nitrous oxide use in rocket propulsion applications is quite limited compared to the other industries and thus its effect on the global warming is negligible.

B) Chemical Properties

Nitrous oxide is a well known oxidizing agent. With only 36% oxygen in the molecule by mass, it is not a highly effective oxidizer. It has a moderate Isp performance which is approximately 30 seconds lower than LOX when they are burned with most common fuels. Nitrous oxide has a positive heat of formation and decomposes into the reference species N_2 and O_2 by releasing substantial heat. Even though this inherent feature of N_2O helps the Isp performance and allows for use in the monopropellant mode, it also introduces the most important safety hazard associated with this substance.

The slightly polar nitrous oxide is a highly effective solvent for hydrocarbons. Its use as a solvent has been quite limited due to safety concerns. The solvent characteristic also introduces significant material compatibility problems.

C) Biological Properties

At low concentrations nitrous oxide is mildly toxic causing central nervous system, cardiovascular, hepatic, hematopoietic, and reproductive effects in humans[8]. Due to its effect on the nervous system, N_2O is sometimes referred to as "Laughing gas". Nitrous oxide is commonly used as an anesthetic (mixture with 20-30% oxygen by mass) and analgesic (mixture with 50% oxygen by mass) agent in medicine and dentistry.

Neurotoxic effects of N_2O occur after acute exposure to concentrations of 80,000 to 200,000 ppm and above. Effects include slowed reaction times and performance decrements[8]. Acute exposure to nitrous oxide concentrations of 400,000 to 800,000 ppm may cause loss of consciousness. Long-term occupational exposure has been associated with numbness, difficulty in concentrating, paresthesias, and impairment of equilibrium[8].

D) Uses for Nitrous Oxide

The common uses for N_2O are summarized in Table 2. Note that for all applications, other than rocket propulsion, nitrous oxide is typically used in small quantities. Typically a standard compressed gas cylinder (less than 60 lb N_2O holding capacity) contains sufficient material limiting the potential hazard. Rocket propulsion is unique in the sense that large quantities of nitrous oxide is stored at room temperature (in flight tanks or run tanks) and consumed at a very fast rate. The fact that light weight flight tanks are not DOT rated vessels adds to the hazard.

Table 2: Uses of Nitrous Oxide.

General Use	Industry
Oxidizer	Rocket propulsion, motor racing
Anesthetic and analgesic	Medical and Dentistry
Gas generator	Airbags, rocket propulsion
Aerosol propellant	Culinary use (in whip cream dispensers)
Etchant	Semiconductor industry
Solvent	Chemical Industry
High Enthalpy Wind Tunnel	Aerospace (Experimental)
Gas Laser	Aerospace/Defense (Experimental)

IV) Accidents Related to Nitrous Oxide Decomposition

Even though nitrous oxide is a very widely used material, the number of serious accidents caused by its decomposition is quite limited. In this section, we include a brief discussion of some of these accidents and their suspected root cause in order to gain a perspective on the overall safety hazard associated with this energetic material. Note that we have not made an attempt to generate a comprehensive list of the N_2O decomposition related accidents. Only the mishaps reported by a reliable source are included in the following list.

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1) During transfer of N_2O from a source cylinder to several smaller cylinders, heating of the source cylinder, which was made out of carbon steel, with an open flame resulted in the decomposition and the rupture of the source vessel[9]. It is possible that rust (iron oxide which is a catalyst for N_2O decomposition) that existed in the source cylinder played a role in the ignition process.

2) A welding repair on or near a 6 ton N_2O tank resulted in a large explosion[10].

3) The use of nitrous oxide mixed with polar solvent modifiers such as ethanol for supercritical fluid extraction or chromatography have resulted in explosions. In one case a mixture of N_2O with 9% ethanol at 40 C and 2100 psi have spontaneously exploded in a stainless steel fitting with an internal volume of 1 milliliter[11]. This case clearly demonstrates the great hazard associated with N_2O contaminated with hydrocarbons.

4) A sub cooled N_2O tank truck exploded in Eindhoven NL[12]. It is believed that following the depletion of the liquid in the truck tank, the pump overheated igniting the vapor in the lines. The flame apparently flashed back into the tank resulting in the rupture of the vessel.

5) Several hybrid rocket ground test accidents have been reported for which the tank ruptured following a chemical explosion. When the liquid in the run tank is depleted, the hot combustion gases could flow back (possibly due to a pressure spike in the combustion chamber) into the tank igniting the N_2O vapor.

6) As discussed earlier, nitrous oxide is widely used in medical applications. An extensive number of accidents that took place in the operating theater have been reported in the literature (i.e. Ref. 13). Three of these are fatal cases. Most of the medical accidents are intestinal explosions which took place during colonoscopy when diathermy is used in the operation. The high concentration of H_2 and CH_4 that naturally exists in the colon and the intestines plays a critical role in the reported events. Note that the concentration of N_2O in body cavities increases to very high levels (more than 50% by mass) in less than 45 minutes after the application of N_2O based anesthetic mixture.

7) SPG has experienced several explosions in the oxidizer feed system of its 250 lb class N_2O motor. The cause of these accidents is believed to be the flow of hot gases back into the feed lines. None of these explosions (some of which produced pressure spikes as high as 3,000 psi) propagated into the tank since the access to ullage was blocked by liquid N_2O in the vertical configuration used in the testing.

8) In 1999, a car installed with a nitrous oxide supercharging system has exploded in the garage. Apparently the bottle heater was accidentally left on and the relief valve on the tank malfunctioned.

9) A composite run tank containing nitrous oxide violently exploded during a cold flow test at Scaled Composites' Mojave test facility in July 2007. Investigation results have not yet been published.

The number of serious accidents within the long history of nitrous oxide use is quite limited. However evaluation of the decomposition hazard for large scale propulsion systems, which is a relatively new use for this material, is critical in the design of such systems and is the subject of the rest of this paper.

V) Nitrous Oxide Decomposition Hazard in Propulsion Systems

In this section we briefly describe the potential hazard associated with N_2O decomposition in different components of a propulsion system. These discussions are applicable to liquid and hybrid rocket systems.

A) N_2O Decomposition in the Oxidizer Tank

Arguably the most important mode of decomposition hazard is associated with the oxidizer tank. Due to the large quantities of N_2O in the tank ullage, a decomposition process in the tank could potentially produce large explosions. This is especially a problem for propulsion systems with closely coupled oxidizer tank and combustion chamber. For such systems, at the end of the liquid burn, the hot injector could potentially

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heat the nitrous vapor in its vicinity and start a deflagration wave that would propagate freely in the tank. Such a situation is illustrated in Figure 1. Note that for pure nitrous oxide in a closed vessel at 300 K, complete decomposition will result in a 20 fold increase in the tank pressure (a number much larger than the safety factor of all flight and run tanks used in propulsion). In fact this indicates that even a partial decomposition could lead to a structural tank failure and loss of mission. Unfortunately the decomposition hazard increases with increasing system scale due the unfavorable surface to volume ratio scaling.
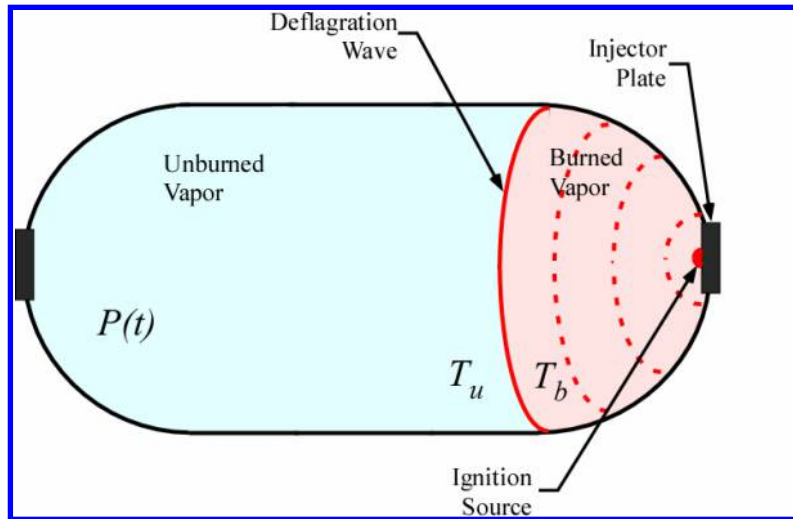
Figure 1: Decomposition wave propagation in oxidizer tank.

The two methods that can be implemented to mitigate this great hazard are 1) Dilution of the ullage with an inert gas such as helium (supercharging) and 2) Incorporation of a properly designed burst disk to limit the overpressurization in the case of ignition in the ullage.

B) Decomposition in the Feed System

The decomposition of nitrous oxide in the oxidizer feed lines is commonly observed in rocket applications. The decomposition reactions in the relatively small volume of the feed system result in an uncontrolled exponential growth in pressure. The chemically induced high pressures generally result in the structural failure of the elements in the feed system. The two common ignition sources are

1) Dead volumes in the feed lines (i.e. Tee fittings in the feed line) are prone to adiabatic compression heating.
2) Hot gases generated by the igniter flows back into the feed lines before the nitrous oxide is introduced. When the oxidizer valve opens, the incoming nitrous oxide mixes with the hot fuel rich gases generated by the igniter and results in a decomposition reaction in the feed lines.

The following methods are recommended to mitigate this particular mode of decomposition hazard: 1) minimize the dead volumes in the feed lines, 2) slow down the valve opening rate and 3) prevent hot gases from the igniter from flowing back into the feed lines.

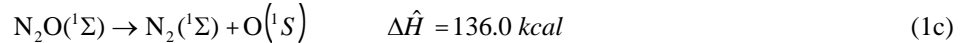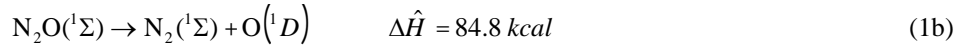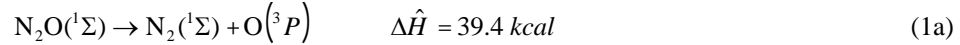## C) Uncontrolled Decomposition in the Combustion Chamber

If a large quantity of nitrous oxide is accumulated in the combustion chamber before the igniter action, a subsequent ignition could result in a chemical explosion and an extreme overpressurization in the combustion chamber. In many cases this kind of a "Hard start" generates high transient loading on the combustion chamber structures and might lead to the loss of mission. The possibility of a "Hard start" can easily be eliminated by adjusting the delay between the oxidizer valve opening and ignition signals in the control system.

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VI) Nitrous Oxide Decomposition Physics

Nitrous oxide is a triatomic linear molecule with the asymmetrical NNO configuration[14]. The electronic structure can be best represented by assuming equal contributions from the resonant structures[14].

$$:\overset{-1}{N}=\overset{+1}{N}=\overset{..}{O}: \qquad :N\equiv\overset{+1}{N}-\overset{..}{\underset{..}{O}}^{-1}$$

Early work has shown that nitrogen atoms are not formed during the decomposition process, which indicates that the decomposition takes place by the break-up of the NO bond. The following reactions, each corresponding to a different electronic state for the atomic oxygen, are possible.

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O\left(^3P\right) \qquad \Delta\hat{H} = 39.4\ kcal \tag{1a}$$

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O\left(^1D\right) \qquad \Delta\hat{H} = 84.8\ kcal \tag{1b}$$

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O\left(^1S\right) \qquad \Delta\hat{H} = 136.0\ kcal \tag{1c}$$

The measured activation energy for the nitrous oxide decomposition of approximately 58 kcal/mole, rules out the last two reactions which require significantly more energy. This indicates that the decomposition of nitrous oxide follows the nonadiabatic spin-forbidden elementary unimolecular reaction.

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O\left(^3P\right) \tag{1a}$$

Note that this reaction requires a change in the multiplicity (from the singlet ground state for the N_2O molecule to a triplet state in atomic oxygen) which is a forbidden transition in quantum mechanics. Due to its interesting spin forbidden nature and also the relatively simple structure of N_2O, this reaction has been the subject of many theoretical studies.

The earliest effort was by Stearn and Eyring[15] who calculated the reaction rate using the unimolecular theory modified for the effect of spin-forbidden transition. Note that since the reaction 1a requires a change in multiplicity, it does not strictly follow the classical unimolecular theory. The rate is determined to be 2 orders of magnitude slower compared to a normal unimolecular reaction due to the reduction in the transmission coefficient induced by the necessary change from the singlet state to the triple state.

The nonrelativistic Born-Oppenheimer potential energy surfaces as a function of the N-O bond distance is shown in Figure 2 for the singlet and triplet states of N_2O[16]. Note that the singlet ground state is represented by an attractive-repulsive potential for which the stable N-O bond distance for the N_2O molecule corresponds to the minimum in the potential curve. All triplet states are repulsive and two of them are degenerate (actually separated by a negligible amount of energy). Thus only two potential curves are shown in Figure 2 to represent the triplet states.

The transition between the singlet and triplet states takes place at the intersection point as shown in Figure 2. An activated complex can be defined at this state and the activation energy for the decomposition reaction can also be determined from the energy difference between the activated complex and the N_2O molecule in the ground state. For the potential surfaces given in Ref 16 and shown in Figure 2, the activation energy is approximately 60 kcal, a number very close to the measured activation energy of 58 kcal for this reaction. The activation energy, E_a, and the enthalpy of reaction, $\Delta\hat{H}$ are marked in the energy diagram shown in Figure 2.

It is important to note that every system crossing the activated state will not complete its transition. The additional energy barrier at the point of crossing that needs to be overcome (between the states of different multiplicity) is induced by the spin-orbit interactions (which are not included in the potential curves shown in Figure 2). The transmission coefficient which is related to the probability of transition at each crossing has been first calculated by Stearn and Eyring[15] with use of the Landau-Zener formula. In this formulation, the transmission coefficient which is a number less than one, multiplies the unimolecular expression for the

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reaction rate and thus successfully explains the abnormally slow reaction rates for the unimolecular decomposition of nitrous oxide.
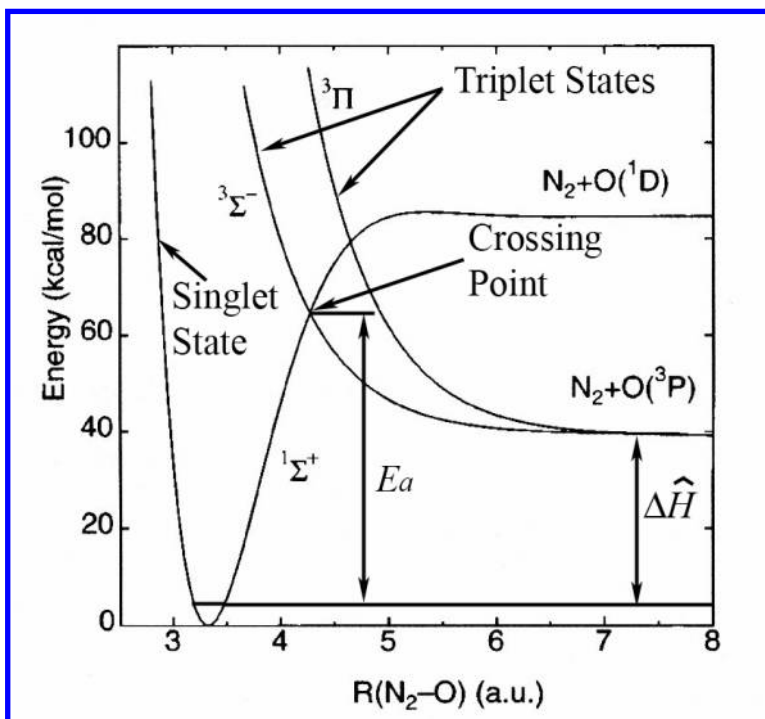
Figure 2: Potential energy for the N_2O molecule as a function of the N-O bond length for the singlet and triplet states (Adapted from Ref. 16).

In the more recent literature, an extensive number of classical and quantum mechanical molecular dynamics simulations have been reported[16, 17, 18 and 19]. The primary objective for these studies has been to gain more insight on the spin forbidden unimolecular decomposition of this relatively simple molecule and to test and benchmark the molecular dynamic models using the well established data for the N_2O decomposition reaction. For example, Marks and Thompson[17] have investigated the effect of energizing different vibrational modes of the N_2O molecule on the decomposition process. They have shown that the stretching modes are preferred over the bending modes in terms of decomposition dynamics.

The abnormally low unimolecular reaction rate for N_2O partly induced by the spin-forbidden processes plays an important role in the relative safety for this commonly used material compared to the other substances that decomposes following unimolecular exothermic reactions (i.e. H_2O_2).

VII) Kinetics of Nitrous Oxide Decomposition

It is well established that nitrous oxide exothermically decomposes into the reference species, O_2 and N_2, following the global reaction.

$$N_2O \rightarrow N_2 + 1/2\,O_2 \qquad \Delta\hat{H}_G = -19.61\,kcal \qquad (2)$$
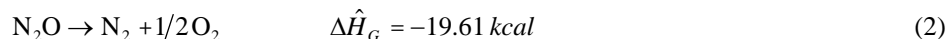
As it will be shown later in this section, the thermal decomposition reaction of N_2O reaches appreciable rates at temperatures around 850K.

The kinetics of decomposition is critical in establishing the ignition and explosion characteristics of this material. In this section, we review the information that exists in the open literature and outline a detailed set of reaction mechanisms that can be used to approximate the decomposition kinetics for nitrous oxide.

Due to its interesting decomposition physics and relatively simple structure, nitrous oxide has been the subject of an extensive number of studies[20-30]. The earliest notable experimental results on N$_2$O decomposition at low pressures have been reported by Hinshelwood and Burk[20]. Hunter[21] and Lewis and Hinshelwood[22] have measured the decomposition rate at elevated pressures and have investigated the effect of pressure on the reaction order. Later Lindars and Hinshelwood[23 and 24] extended their studies to include a more detailed reaction mechanism and the effects of the surface reactions. Kaufman *et al*[25] have investigated the formation of NO during the decomposition process of nitrous oxide. The decomposition mechanisms that they have recommended are still widely accepted and have also been adopted in this study. Fishburne and Edse[26] have investigated the two parallel elementary reactions that take place between N$_2$O and atomic oxygen in the context of N$_2$O decomposition. Glarborg *et al*[28] have established the efficiencies for various molecules as collision partners. An excellent review of N$_2$O decomposition kinetics is given in Ref. 29.

As discussed in the previous section the decomposition of the nitrous oxide molecule follows the elementary reaction.

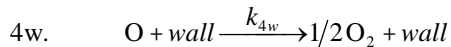$$1. \qquad N_2O + M \xrightarrow{k_1} N_2 + O + M \qquad\qquad \Delta\hat{H} = 39.4\ kcal$$

Here M is an arbitrary collision partner that exists in the system. Note that each collision partner has a different efficiency resulting in different rate constants. As will be discussed later in this section, this distinction looses its practical significance at high pressures common to most propulsion systems.
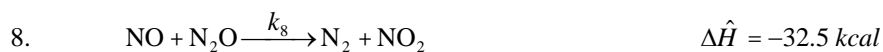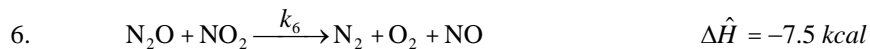
The atomic oxygen radicals produced by the decomposition process (reaction 1) react with N$_2$O following the two well established parallel reactions[26 and 29].

$$2. \qquad N_2O + O \xrightarrow{k_2} NO + NO \qquad\qquad \Delta\hat{H} = -35.9\ kcal$$

$$3. \qquad N_2O + O \xrightarrow{k_3} N_2 + O_2 \qquad\qquad \Delta\hat{H} = -78.9\ kcal$$

The rates for these two reactions are reported to be very close over a wide range of temperatures and following Blauch's recommendation[29], equal rates are assumed in our formulation (see Table 4). The atomic oxygen radical can also be eliminated from the system by the termolecular homogeneous recombination reaction or by the heterogeneous recombination reaction that takes place on solid surfaces.

$$4. \qquad O + O + M \xrightarrow{k_4} O_2 + M \qquad\qquad \Delta\hat{H} = -118.0\ kcal$$

$$4w. \qquad O + wall \xrightarrow{k_{4w}} 1/2\,O_2 + wall$$

Even though the set of elementary reactions given by equations 1-4w are the most important ones in establishing the decomposition kinetics of nitrous oxide, the following reactions are also believed to play some role, especially at the later stages of the reaction[25, 26 and 29]. Thus they are included in the detailed mechanism.

$$5. \qquad NO + O + M \xrightarrow{k_5} NO_2 + M \qquad\qquad \Delta\hat{H} = -71.4\ kcal$$

$$6. \qquad N_2O + NO_2 \xrightarrow{k_6} N_2 + O_2 + NO \qquad\qquad \Delta\hat{H} = -7.5\ kcal$$

$$7. \qquad NO_2 + O \xrightarrow{k_7} NO + O_2 \qquad\qquad \Delta\hat{H} = -45.8\ kcal$$

$$8. \qquad NO + N_2O \xrightarrow{k_8} N_2 + NO_2 \qquad\qquad \Delta\hat{H} = -32.5\ kcal$$

It can be shown that reaction 5 is important in the self-limiting process for the production of NO, particularly at large conversion rates[25].

A simplified, but highly accurate representation of the mechanism can be obtained by only considering reactions 1, 2 , 3, 4 and 4w. For this reduced set, the dynamic equation for the molar concentrations of N_2O and O can be written as.

$$\frac{d[N_2O]}{dt} = -k_1[N_2O][M] - (k_2 + k_3)[N_2O][O] \tag{3}$$

$$\frac{d[O]}{dt} = k_1[N_2O][M] - (k_2 + k_3)[N_2O][O] - k_4[O]^2[M] + k_{4w}[O] \tag{4}$$

The steady-state assumption, $d[O]/dt \cong 0$, results in the following expression for the concentration of the atomic oxygen radical.

$$[O]_{ss} = \frac{k_1[N_2O][M]}{(k_2 + k_3)[N_2O] + k_{4w}} \tag{5}$$

Note that the effect of reaction 4 has been ignored since the probability of the termolecular collisions is expected to be small. For systems with small surface to volume ratios the k_{4w} term can also be neglected, resulting in the following dynamic equation for the N_2O molar concentration.

$$\frac{d[N_2O]}{dt} = -m k_1[N_2O][M] \tag{6}$$

Note that for this particular system, for which the oxygen recombination reactions are negligible, the stoichiometry of the overall reaction, m, can be shown to be 2.

In the other extreme case of fast recombination reactions for atomic oxygen, the reactions 2 and 3 become irrelevant and the stoichiometry of the reaction, m, becomes one. For most practical cases $1<m<2$ is expected.

Lindemann's Theory:

Using Lindemann's theory[31], reaction 1 can further be broken down to include the formation of an activated complex by molecular collisions, the backwards deactivation reaction and the decomposition reaction associated with the activated complex.

1a. $\quad N_2O + M \xrightarrow{k_a} N_2O^* + M$

1-a. $\quad N_2O^* + M \xrightarrow{k_{-a}} N_2O + M$

1b. $\quad N_2O^* \xrightarrow{k_b} N_2 + O$
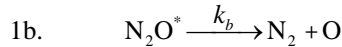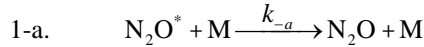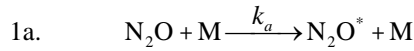
Following the reaction mechanism given by equations 1a, 1-a and 1b, the dynamic equations for the N_2O and the activated complex N_2O^* can be written as

$$\frac{d[N_2O]}{dt} = -k_a[N_2O][M] + k_{-a}[N_2O^*][M] \tag{7}$$

$$\frac{d[N_2O^*]}{dt} = -k_{-a}[N_2O^*][M] + k_a[N_2O][M] - k_b[N_2O^*] \tag{8}$$

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Following the implementation of the steady state approximation for the activated complex, one can obtain the steady state concentration.

$$\left[N_2O^*\right]_{ss} \cong \frac{k_a\left[N_2O\right]\left[M\right]}{k_b + k_{-a}\left[M\right]} \tag{9}$$

Substitution back in Eq. 7 yields the rate constant for reaction 1 as a function of molar concentration (i.e. system pressure).

$$k_1 \cong \frac{k_a k_b}{k_b + k_{-a}\left[M\right]} \tag{10}$$

High Pressure Limit:

Using the approximation, $k_{-a}\left[M\right] >> k_b$, at high pressures and combining Eqs. 6 and 10 results in.

$$\frac{d\left[N_2O\right]}{dt} = -m k_1^\infty \left[N_2O\right] \tag{11}$$

The high pressure rate constant is defined as $k_1^\infty \equiv k_a k_b / k_{-a}$. Note that at high pressures the reaction is first order and the concentration of the collision partner, [M], does not affect the reaction rate. In other words, at high pressures, the rate that the activated complexes are formed by molecular collisions is fast and the rate controlling step is decomposition given by reaction 1b. The following formula for the high pressure reaction constant, which is recommended in the temperature range of 900-2100 K, shall be used in this study[29].

$$k_1^\infty = A_r\, e^{-E_a/R_u T} = 1.3\, \text{x}\, 10^{11}\, e^{-58,000/R_u T} \quad \text{sec}^{-1} \tag{12}$$

Also note that in the high pressure limit, the collision efficiencies with different molecules do not have to be considered eliminating much of the ambiguity in the kinetics calculations.

Low Pressure Limit:

Note that at low pressures $k_{-a}\left[M\right] << k_b$. In this limit, combining Eqs. 6 and 10 results in.

$$\frac{d\left[N_2O\right]}{dt} = -m k_1^o \left[N_2O\right]\left[M\right] \tag{13}$$

Here the low pressure rate constant has been defined as $k_1^o \equiv k_a$. Note that at low pressures the reaction rate is controlled by the collision frequency and thus the reaction is second order. For the collision partner of N_2O and in the limited temperature range of 900-1050 K, the following reaction rate is recommended by Baulch *et al*[29].

$$k_1^o = A_r\, e^{-E_a/R_u T} = 2.7\, \text{x}\, 10^{15}\, e^{-59,200/R_u T} \quad cm^3\, mole^{-1}\, \text{sec}^{-1} \tag{14}$$

The relative efficiencies for various collision partners that are important in propulsion systems, are listed in Table 3[30]. Note that the relative efficiency data from different sources is highly conflicting[29] and the listed efficiencies should only be taken as very rough estimates.

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Table 3: Efficiencies for various collision partners.

| M=N_2O	He	O_2	N_2	CO_2
1	1.0	0.21	0.26	1.2

At intermediate pressure levels, the reaction constant follows the fall off curve.

$$k_1 = \frac{k_1^{\infty} k_1^{o} [M]}{k_1^{\infty} + k_1^{o} [M]}$$

(15)

This behavior has been shown experimentally by Lewis and Hinshelwood[22]. Figure 3 shows the reaction constant as a function of pressure. As indicated in the figure, the kinetics is primarily first order for pressures larger than 40 atm (590 psi). Thus for most propulsion applications the N_2O decomposition reaction can be assumed to be first order and the kinetics can be accurately captured by the following equation (*m=2* assumed).

$$\frac{d[N_2O]}{dt} = -m A_r e^{-E_a/R_u T} [N_2O] = -2.6 \times 10^{11} e^{-58,000/R_u T} [N_2O] \quad sec^{-1}$$

(16)
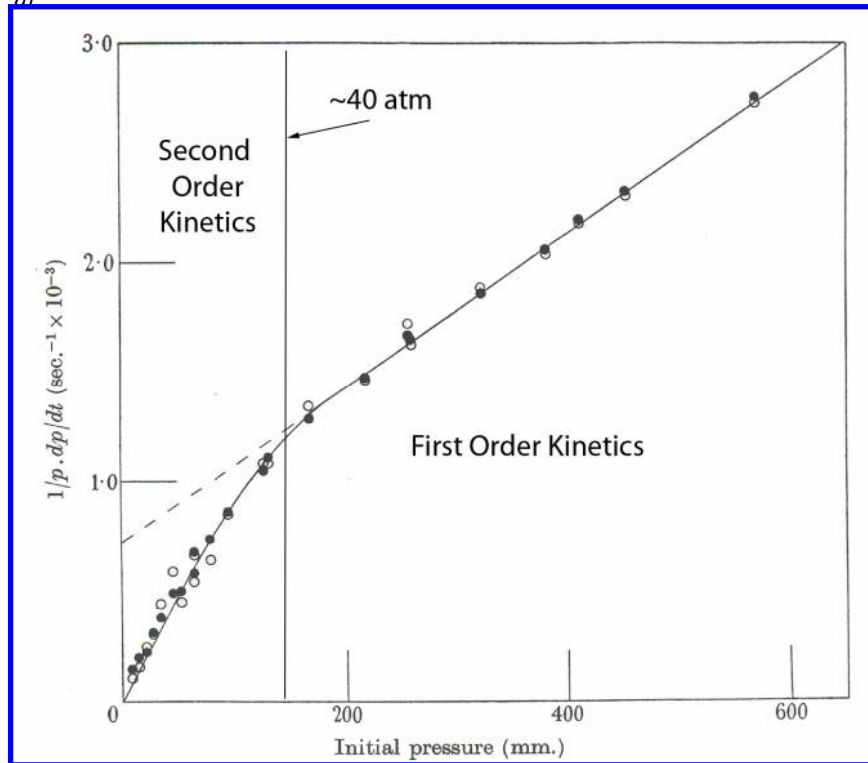
Figure 3: The reaction rate as a function of system pressure for N_2O decomposition (adapted from Ref. 22).

Detailed Kinetic Calculations:

Detailed kinetic calculations have been conducted using the set of elementary reactions 1-8. The kinetic data used in the calculations have been summarized in Table 4.

As shown in Figure 4, the simplified kinetics given by Eq. 16 is a reasonably close approximation to the calculations conducted using the detailed kinetics model. It is determined that the surface recombination reaction for the atomic oxygen is critical in establishing the accuracy of the simplified model. For the particular case shown in Figure 2, a k_{4w} value of 0.2 has been used in the calculations. It has been

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determined that as the k_{4w} value increases the decomposition rate slows down and the prediction by the simplified kinetics expression becomes less accurate. This effect is due to the change in the stoichiometry of the reaction, m, by the removal of the atomic oxygen from the system. It has also been determined that the homogenous recombination reaction given by equation 4 is not as effective in the removal of the atomic oxygen due to the low probability of this termolecular reaction. We could not find any reliable rate data for reaction 6 in the open literature. Thus k_6 has been arbitrarily set equal to the rate of reaction 7. Fortunately, an analysis showed that the end results are quite insensitive to the assumed rate of reaction 6. Namely, changing k_6 from a value of zero to 10^{13} had a very small of effect on the time variation of the N_2O concentration.

Table 4: Reaction rate data for N_2O decomposition kinetics.

	Reaction	Rate constant, k**	Source
1	$N_2O \rightarrow N_2 + O$ *	$1.3 \times 10^{11} \exp(-58,000/R_uT)$	Baulch *et al*[29]
2	$N_2O + O \rightarrow NO + NO$	$1.0 \times 10^{14} \exp(-28,000/R_uT)$	Baulch *et al*[29]
3	$N_2O + O \rightarrow N_2 + O_2$	$1.0 \times 10^{14} \exp(-28,000/R_uT)$	Baulch *et al*[29]
4	$O + O + M \rightarrow O_2 + M$	$6.81 \times 10^{12} (2,200/T)^{1.22}$	Fishburne and Edse[26]
5	$NO + O + M \rightarrow NO_2 + M$	$1.1 \times 10^{15} \exp(1,870/R_uT)$	Baulch *et al*[29]
6	$NO_2 + NO_2 \rightarrow N_2 + O_2 + NO$	Set equal to reaction 7 (insensitive)	
7	$NO_2 + O \rightarrow NO + O_2$	$3.91 \times 10^{12} \exp(239/R_uT)$	Glassman[32]
8	$NO + N_2O \rightarrow N_2 + NO_2$	$1.0 \times 10^{14} \exp(-50,000/R_uT)$	Glassman[32]

*High pressure limit, **Units are cm^3, mole, cal

The other important observation from the detailed kinetics simulations is the production of large concentrations of NO. Note that NO production in the N_2O decomposition process has been measured by Lindars and Hinshelwood[23] and has been modeled by Kaufman[25]. The results of the detailed kinetics model presented in this paper are consistent with their findings. Finally a small but finite amount of NO_2 is formed in the course of the decomposition process.
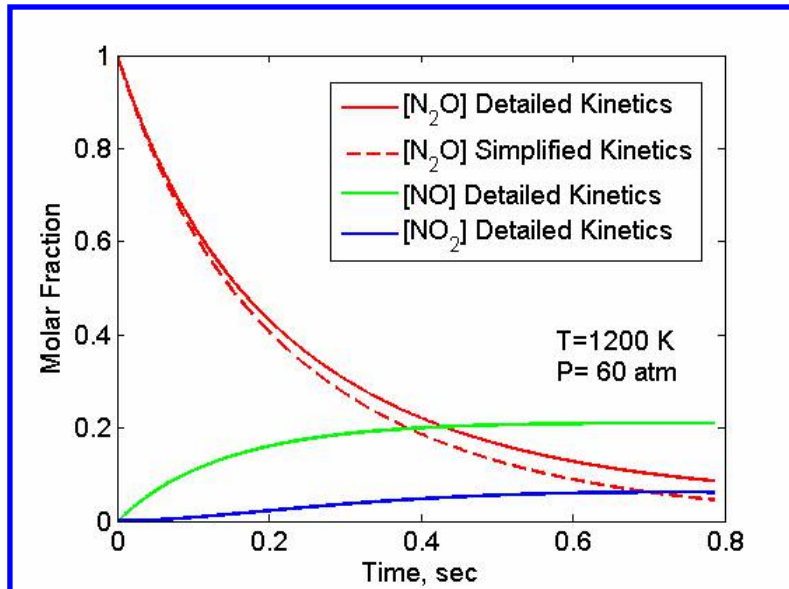
Figure 4: Detailed kinetics calculation results for N_2O decomposition at 1200 K and 60 atm.

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Characteristic Decomposition Time

The characteristic decomposition time, $\tau_d \equiv 1/k_1^\infty$ for N_2O at high pressures (> 40 atm) has been plotted as a function of temperature in Figure 5. As can be deduced from the figure, no appreciable decomposition takes place for temperatures less than 850 K. The time scale for decomposition reduces exponentially with temperature and at temperatures larger than 1500 K reaches the millisecond scales.
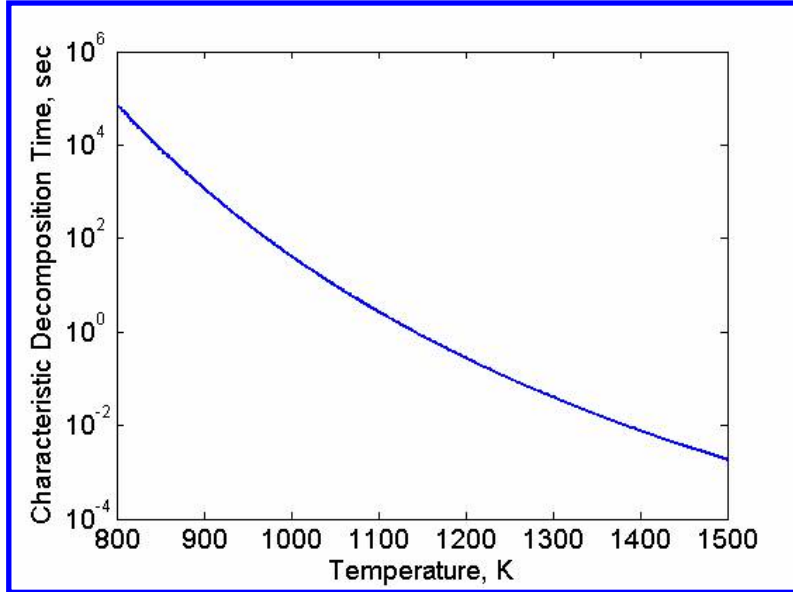

Figure 5: Characteristic decomposition time as a function of temperature at pressures larger than 40 atm.

Comparison to H_2O_2 Decomposition

It is worth while to compare the decomposition characteristics of the two commonly used storable oxidizers (and monopropellants), nitrous oxide and hydrogen peroxide (H_2O_2). It is well known that H_2O_2 also decomposes exothermically following the global reaction[33].

$$H_2O_2 \rightarrow H_2O + 1/2\,O_2 \qquad \Delta\hat{H}_G = 23.44 \; kcal \qquad (17)$$
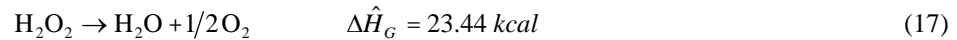
Note that the energies associated with the decomposition of 100% H_2O_2 and N_2O are 689 cal/g and 446 g/mol, respectively. The dynamic equation for the molar concentration of H_2O_2 also follows the first order kinetics in the high pressure limit.

$$\frac{d\,[H_2O_2]}{dt} = -\bar{k}_1^\infty [H_2O_2] \quad sec^{-1} \qquad (18)$$

The following high pressure vapor phase reaction rate constant is recommended by Ref. 33.

$$\bar{k}_1^\infty = 3.16 \times 10^{14} \; e^{-48,500/R_u T} \quad sec^{-1} \qquad (19)$$

Eq. 19 is reported to be accurate in the temperature range of 730-1230 C.

For comparison purposes, the high pressure rate constants for N_2O and H_2O_2 are plotted as a function of temperature in Figure 6. As shown in the figure, the reaction rate constant for H_2O_2 is almost six orders of magnitude larger that the rate constant for N_2O decomposition. Approximately half of this difference is originated by the lower value of the reaction rate coefficient A_r (primarily due to the spin forbidden

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transition of N_2O as discussed in the previous section) and the other half is due to the lower activation energy associated with the decomposition of H_2O_2 (48,500 cal/mole versus 58,000 cal/mole for N_2O).
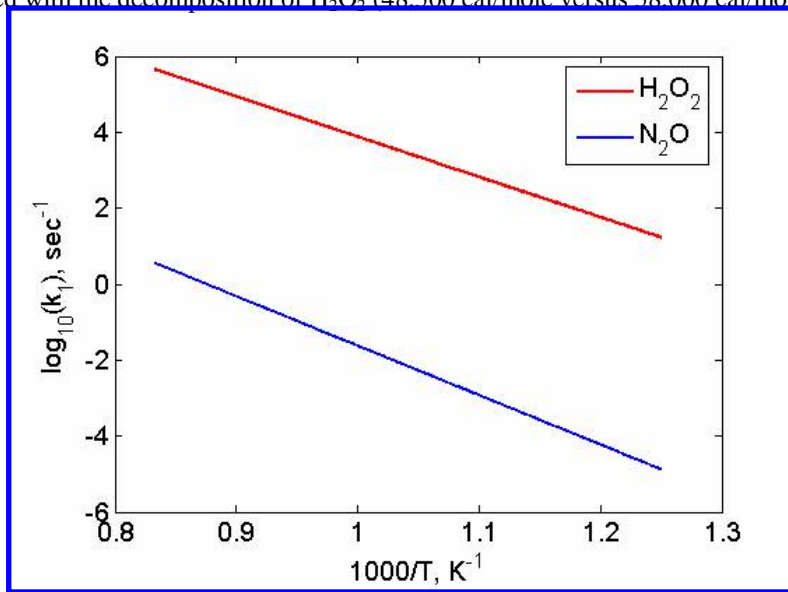
Figure 6: High Pressure decomposition reaction rate constant for N_2O and H_2O_2.

Figure 6 clearly shows the relative safety of nitrous oxide compared to hydrogen peroxide. Even though both materials release comparable levels of energy as they decompose, the significantly reduced rate of decomposition makes nitrous oxide a much less sensitive material.

The other major safety related distinction between these two commonly used oxidizers is the fact that the decomposition reaction in liquid phase H_2O_2 is possible, whereas all attempts, as they have been reported in the open literature, to ignite liquid N_2O have failed[4 and 34].

VIII) Homogenous and Local Thermal Ignition

The ignition of nitrous oxide vapor can take place homogenously when the material is uniformly heated to a temperature larger than its autoignition temperature or locally when enough energy (and free radicals) is locally introduced to the vapor at lower temperatures such that a self sustaining deflagration wave (flame) can start to propagate in the medium. In this section both ignition processes for the nitrous oxide decomposition shall be discussed and ignitability of N_2O will be evaluated.

A) Homogenous Ignition

When nitrous oxide is uniformly elevated to high enough temperatures, the decomposition reactions start to be important. At a certain temperature, the heat produced by the exothermic reactions exceeds the heat loss to the surroundings and an increase in the temperature is observed. A slow increase in temperature, induction period, is typically followed by an exponential growth period (explosion). It is fair to say that this mode of ignition is highly unlikely in the oxidizer tank ullage, since elevating the ullage temperature to the relatively high autoignition temperatures of nitrous oxide requires vast amounts of heat (or compression work) which is not readily available in a typical system. The areas that the homogenous ignition is likely to play a significant role are the feed lines and particularly the dead volumes in the feed lines which could be subject to appreciable increase in temperature due to gas compression effects.

In this section we outline a model that can be used to establish the homogenous ignition characteristics of nitrous oxide in a closed volume. For simplicity the following simplifying assumptions have been employed:

- The reaction is first order and follows the simplified kinetics given by Eq. 16.

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- The reaction takes place in a closed volume with no mass transfer through its boundaries.
- The closed volume is assumed to be cylindrical in shape with a hydraulic diameter of D and a surface area of A.
- An ideal mixture is assumed. However the real gas behavior associated with the nitrous oxide component is approximated by the use of a compressibility factor, z_{N2O} applied to the nitrous term.
- The initial N_2O vapor temperature, T_o, is assumed to be uniform in the vessel.
- The wall temperature of the vessel, T_w, is assumed to be constant in time. This is a good assumption early in the reaction. Thus the error introduced by this approximation on establishing the ignition boundaries is expected to be small.

Using the preceding assumptions, the energy equation for a reacting vapor/gas mixture in a closed vessel can be reduced to the following non-dimensional nonlinear ordinary differential equation for the temperature.

$$\frac{d\overline{T}}{d\bar{t}} = E_H\left(\bar{t}\right) e^{\frac{T_a}{T_o}\left(\frac{1}{\overline{T}}-1\right)} C_{N2O} - \frac{\hat{c}_{vo}}{\hat{c}_v\left(\bar{t}\right)}\frac{\tau_r}{\tau_c}\frac{\overline{T}-T_w/T_o}{1-T_w/T_o} \tag{20}$$

Using the global reaction one can also obtain the dynamic equations for the species mole concentrations.

$$-\frac{dC_{N2O}}{d\bar{t}} = \frac{dC_{N2}}{d\bar{t}} = 2\frac{dC_{O2}}{d\bar{t}} = e^{\frac{T_a}{T_o}\left(\frac{1}{\overline{T}}-1\right)} C_{N2O} \tag{21}$$

Here the non-dimensional variables are defined as

$$\bar{t} \equiv \frac{t}{\tau_r}, \quad \overline{T} \equiv \frac{T}{T_o}, \quad C_{N2O} \equiv \frac{[N_2O]}{[N_2O]_o}, \quad C_{N2} \equiv \frac{[N_2]}{[N_2O]_o}, \quad C_{O2} \equiv \frac{[O_2]}{[N_2O]_o} \tag{22a}$$

$$E_H\left(\bar{t}\right) \equiv \frac{\Delta\hat{H}_G}{\hat{c}_v\left(\bar{t}\right)T_o}, \quad T_a \equiv \frac{E_a}{R_u}, \quad \tau_c \equiv \frac{4\hat{c}_{vo}T_o[N_2O]_o D}{\pi Nu\,\lambda\left(T_o-T_w\right)A}, \quad \tau_r = \frac{e^{T_a/T_o}}{m\,A_r} \tag{22b}$$

Note that τ_c is the cooling time scale and τ_r is the reaction time scale. The average heat capacity of the gas mixture, $\hat{c}_v$, varies with time, since it is a function of the temperature and the molar fractions of the species. Note that $\hat{c}_{vo}$ is the specific heat of the mixture at $\bar{t}=0$. The Nusselt number is defined as $Nu \equiv hD/\lambda$ where h is the convective heat transfer coefficient, and λ is the coefficient of thermal conductivity for the gas mixture.

For the following set of initial conditions, Eqs. 20 and 21 can easily be integrated numerically to generate the time variations of temperature and species concentrations.

$$C_{N2O}\big|_{\bar{t}=0} = 1, \quad C_{N2}\big|_{\bar{t}=0} = f_{N2}, \quad C_{O2}\big|_{\bar{t}=0} = f_{O2}, \quad \overline{T}\big|_{\bar{t}=0} = 1 \tag{23}$$

Here f_{N2} and f_{O2} represent the non-dimensional molar concentrations of N_2 and O_2 in the mixture at $\bar{t}=0$. A MATLAB based simulation code has been developed to solve this initial value problem. Some of the interesting solutions generated using this code are discussed in the following paragraphs.

First we have considered a pure N_2O system with no heat transfer. Note that this case is representative of a vessel with a large diameter for which the ratio of the times scales, τ_r/τ_c, vanishes, namely convective term in the energy equation becomes negligible compared to the reaction term. Figure 7 shows the

temperature as a function of time for three different initial temperatures for this particular case. One of the most striking observations from this simulation result is the high sensitivity of the induction period to the initial temperature. Even with no heat loss, at temperatures less than 850 K, the induction periods are quite long (> 25 sec). It is fair to state that the critical temperature at which the homogenous ignition of N_2O vapor takes place within a reasonable time period (in the context of propulsion system applications) is around 850 K.

As clearly seen in Figure 7, in the induction period, the reactions are slow and the temperature slowly increases up to the overheating limit, T_M, which can be estimated using the large activation energy asymptotic approximation[35].

$$T_M \cong T_o + \frac{R_u T_o^2}{E_a} = T_o \left(1 + \frac{T}{T_a} \right) \tag{24}$$

Once the system temperature exceeds T_M, explosive behavior is observed. Note that $T = T_M$ is an inflection point of the system.
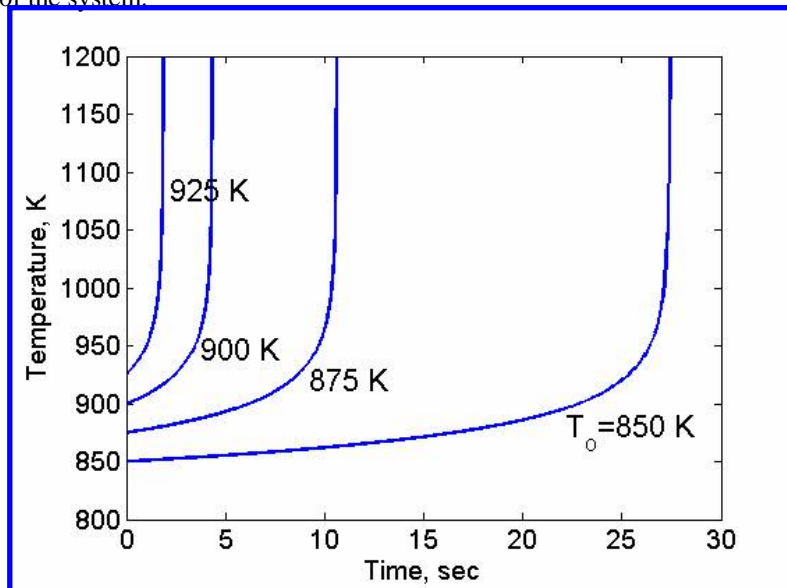
Figure 7: Induction time as a function of initial temperature, no heat loss case.

In practice the total pressure is preferred as a system variable over the molar concentrations. The initial system pressure can be related to the initial molar density of nitrous oxide by the use of the equation of state.

$$P_o = \frac{(z_{N2O} + f_o + f_N) R_u T_o}{V} [N_2O]_o \tag{25}$$

Here z_{N2O} is the compressibility of nitrous oxide vapor at the initial pressure (which can be evaluated at a given pressure and temperature using an equation of state such as Peng-Robinson[36]) and temperature. An ideal mixture is assumed and no compressibility correction has been included for molecular oxygen or molecular nitrogen.

It is useful to establish an explosion boundary that relates the vessel size to the initial temperature and initial pressure. Eq. 20 can be used for this purpose resulting in the following expression for the explosion boundary.

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$$D^2 = \frac{(z_{N2O} + f_{O2} + f_{N2})\, Nu\, \lambda\, R_u\, T_o^2}{\Delta \hat{H}_G P_o\, m\, A_r e^{-T_a/T_M}}\, \frac{T_o}{T_a} \tag{26}$$

Eq. 26 will be used to quantify the explosion boundaries on the *P-T* plane for a range of vessel diameters. For simplicity, the vessels are assumed to have large *L/D* and the initial composition is taken to be pure N$_2$O. Following the recommendation of Ref. 37, a Nusselt number of 5.4 has been used in the calculations for this large *L/D* configuration.

Figure 8 shows the ignition boundaries for three diameters, 0.2 m, 1.0 m and 2.0 m. For the largest vessel, the ignition temperature is in the range of 670-700 K. Note that for temperatures close to the boundary value, the induction times are very long (infinite on the boundary). As discussed in the previous paragraphs, for temperatures less than 850 K, the induction periods are too long to be practical for most propulsion systems.
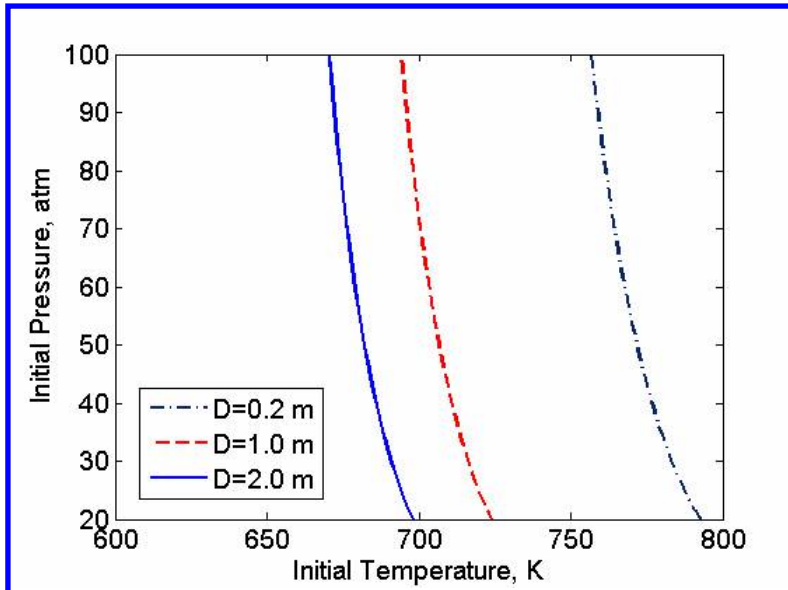
Figure 9: Ignition boundary for cylindrical vessels with varying diameters.
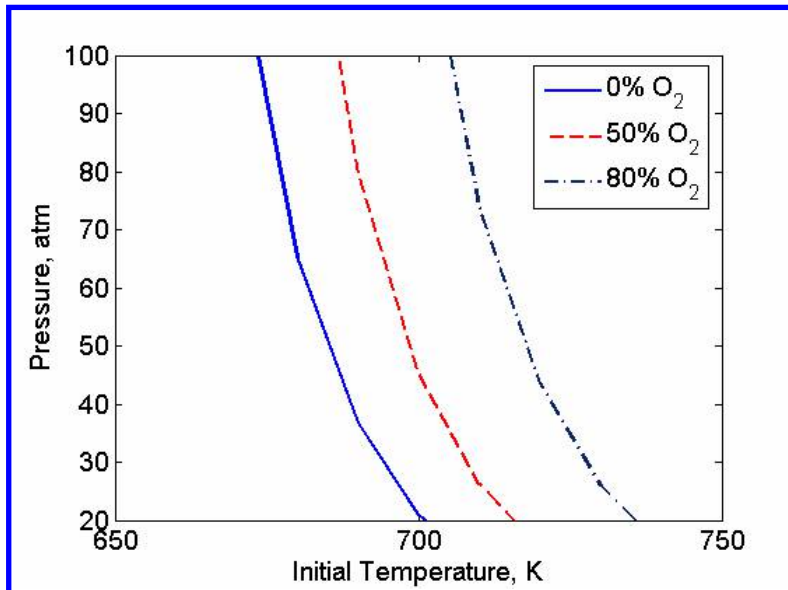
Figure 9: Effect of diluent concentration on the ignition boundary. Vessel diameter 2 m.

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Finally the effect of dilution on the explosion boundary has been demonstrated in Figure 9, which shows the explosion boundaries for a cylindrical vessel with a diameter of 2 m at three oxygen concentration levels, 0%, 50% and 80% by mass. The interesting observation is that the effect of diluents on the ignition boundary is relatively small, approximately a 30 K change for a jump from the 0% to the 80% level. As will be discussed in the following paragraphs, the situation is completely different for the local thermal ignition process.

B) Local Thermal Ignition

Local thermal ignition is the most common ignition mode expected in rocket propulsion applications, since it only requires small quantities of highly localized thermal energy which is readily available in all practical systems. As will be discussed later in this paper, a local ignition would start a self sustained deflagration wave in the N_2O vapor and the heat release and mole gains associated with this process result in an overpressurization of the pressure vessel. The violence of the explosion or the rate of increase in pressure depends on the speed of the deflagration wave. Thus one of the key steps in establishing the pressurization rate is to estimate the laminar flame speed, S_L, in the N_2O vapor at a given pressure and temperature. This can be achieved by using the Zeldovich theory[32]. Specifically, for a first order reaction and a Lewis number of unity, the laminar flame speed can be approximated by the following algebraic equation.

$$S_L = \left\{ \frac{2\,\lambda_f C_{pf} A_r}{\rho_o \overline{C}_p^2} \frac{T_o}{T_f} \frac{n_r}{n_p} \left(\frac{R_u T_f^2}{E_a} \right)^2 \frac{e^{-E_a/R_u T_f}}{\left(T_f - T_o\right)^2} \right\}^{1/2} \tag{27}$$

Here T_f is the adiabatic flame temperature at constant pressure, n_r/n_p is the mole ratio of the reactant to products, λ_f is the coefficient of heat conduction of the decomposition products, C_{pf} is the specific heat of the products and the $\overline{C}_p$ is the average specific heat across the flame thickness and ρ_o is the density of the unburned vapor (or vapor/gas mixture).

Using the simplified kinetics model developed in section VII, we have calculated the laminar flame speed for N_2O as a function of oxygen dilution at three pressure levels, 40, 50 and 60 atmospheres. Note that the simplified first order kinetic model is not valid for pressures below 40 atmospheres. As expected the laminar flame speeds, which are plotted in Figure 10, show a decreasing trend with increasing oxygen mass fraction primarily due to the reduction in the adiabatic flame temperature with dilution. The other interesting observation is that the flame speeds are fairly low, in the range of 10-15 cm/sec even for the undiluted N_2O. This is primarily due to two reasons 1) relatively low adiabatic flame temperatures (deficient reaction energy) and 2) inherently slow kinetics for the decomposition of N_2O as discussed in section VI. The predicted flame speed of 15 cm/sec at 40 atm is in good agreement with the measured flame speed with respect to the unburned gas in pure N_2O as reported in Ref. 4. Finally the figure indicates that the laminar flame speed decreases with increasing pressure. This is consistent with the first order kinetics and theoretically follows the $S_L \propto P_o^{-1/2}$ scaling (for an ideal gas) as can be deduced from Eq. 27. The actual exponent is more negative than -1/2 primarily due to real gas effects. Note that the real gas effects have been partially captured in our calculations by incorporating a compressibility correction for N_2O in the unburned mixture.
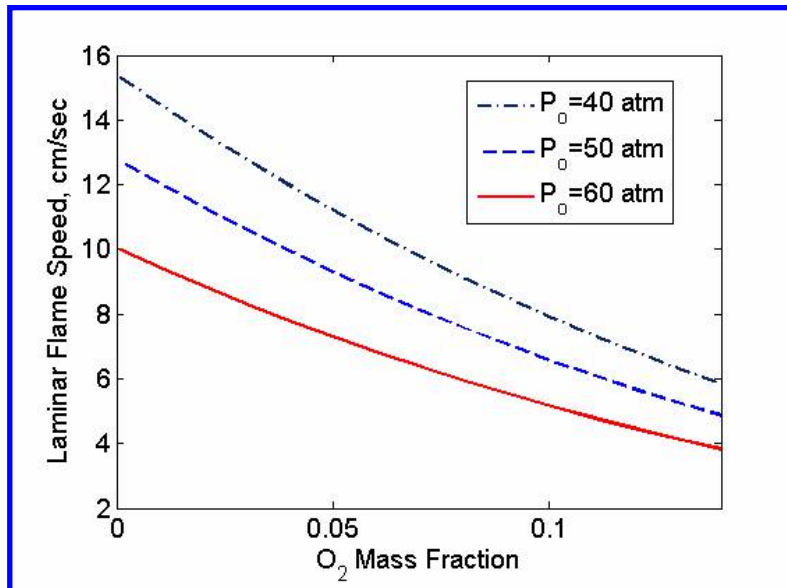
Figure 10: Laminar flame speed for N_2O/O_2 mixtures at three pressure levels.

Figure 11 shows the quenching distance estimate for N_2O/O_2 mixtures at 40, 50 and 60 atm for an initial temperature 300K. Note that the quenching distance for pure N_2O is around 0.7 cm and it increases with increasing level of dilution as expected.
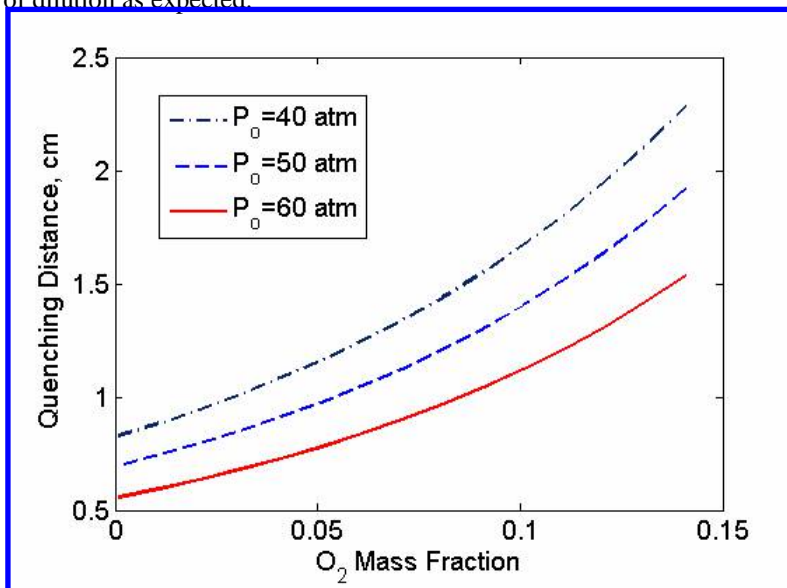

Figure 11: Quenching distance for N_2O/O_2 mixtures at 40, 50 and 60 atm.

Following the method outlined in Ref. 38, the minimum ignition energies for the N_2O/O_2 mixtures have been estimated and plotted for three pressure levels in Figure 12. Note that this simplified calculation methodology for the ignition energy assumes that the thermal energy is instantaneously applied to a spherical kernel with a diameter equal to the quenching distance. Moreover no energy radiation is allowed by the shock waves generated by the sudden expansion in the ignition kernel. In reality the ignition energy is expected to be higher. For example if the heating is too slow the heat conduction into the surrounding medium will result in a loss and increase in the ignition energy. In the other extreme, if the application of the heat is too fast the shock waves will form and convect an appreciable part of the supplied energy to the surrounding medium. These are just two possibilities and in reality there are many other factors that influence the value of the ignition energy. The ignition is a rather complicated process which depends

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heavily on the method (i.e. spark plug, hot plate/rod, hot jet). A detailed description and modeling of the ignition process, which is covered extensively in Ref. 38-40, is beyond the scope of this paper.

As shown in Figure 12, the minimum ignition energy for pure N_2O is in the range of 400-500 mJ. Even though this energy is orders of magnitude higher than the ignition energy for the stoichiometric hydrocarbon/air mixtures, in a typical propulsion system, there exists a substantial number of potential sources of thermal energy at this level. The ignition energy for pure N_2O is measured and reported to be 140 mJ in Ref. 4. Even though the calculated and measured energies are the same order, they are appreciably different. This much difference is not surprising, since the calculations based on our simple model is a rough approximation and the energy measurements are reported in Ref. 4 to be a crude order of magnitude estimate.

Another practical observation from Figure 12 is that the influence of dilution on the ignition energy is significant. Namely, a 10% oxygen dilution results in an order of magnitude increase in the minimum ignition energy. Even though it is not shown in the figure, a 30% dilution with oxygen increases the minimum ignition energy to approximately 500 J, making this mixture virtually impossible to ignite. Finally system pressure has a small but finite influence on the minimum ignition energy, namely increasing pressure results in a reduction in the ignition energy. This trend is primarily driven by the reduction in the quenching distance with increasing pressure.
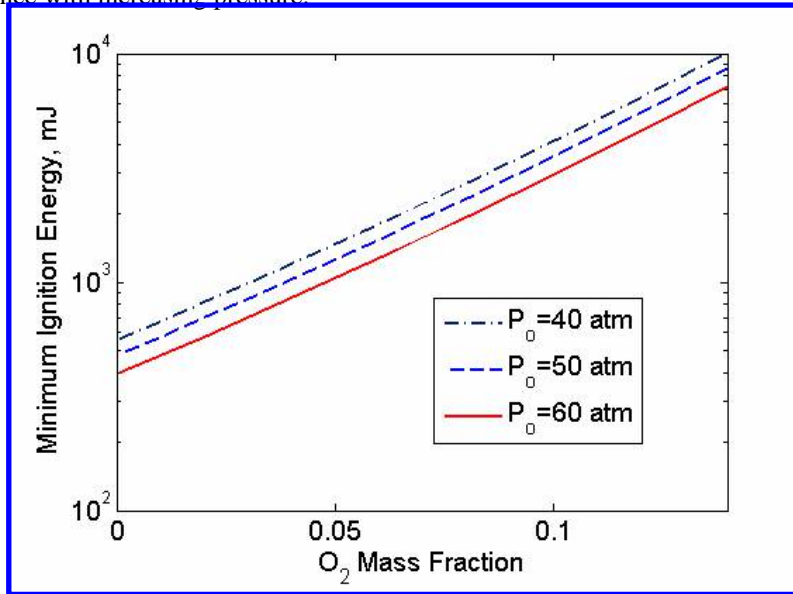
Figure 12: Minimum ignition energy for N_2O/O_2 mixtures at three pressure levels.

Similar results are expected when N_2 is used as the diluent. Helium would be a more effective diluent compared to O_2 or N_2. This is due to the significant increase in the heat conduction coefficient with the introduction of light helium atoms into the mixture.

Table 6: Comparison of N_2O decomposition to stoichiometric CH_4/O_2 and $CH_4/$ Air combustion.

Property	N_2O Decomposition	$CH_4/$ Air Combustion	CH_4/O_2 Combustion
Reaction Order	First order (P>40 atm)	Close to second order	
Reaction Mechanism	Relatively simple	Complex	
Laminar Flame Speed	12* cm/sec	35** cm/sec	327** cm/sec
Quenching Distance	0.7* cm	0.2** cm	0.035** cm
Minimum Ignition Energy	450* mJ	0.45** mJ	0.002** mJ
Flame Pressure Scaling	$S_L \propto P_o^{-0.5}$	$S_L \propto P_o^{-0.1}$	

* Evaluated at 50 atm and 300 K   ** Evaluated at 1 atm and 300 K

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Table 6 has been included in order to compare and contrast the properties of N_2O decomposition to the combustion of stoichiometric methane/oxygen and methane/air mixtures[40]. This table clearly demonstrates that N_2O is much more difficult to ignite and has a much slower deflagration wave speed and is much easier to quench. In short, it is fair to state that the N_2O decomposition is not nearly as intense as the hydrocarbon/oxygen combustion process.

IX) Decomposition Induced Pressure Increase in a Closed Vessel

An important mode of failure is the decomposition of the N_2O vapor in the oxidizer tank. Due to the large quantities of N_2O in the tank ullage, a decomposition process in the tank could potentially produce large explosions. Unfortunately at larger scales the situation gets worse since the surface to volume ratio reduces as the tank size grows. This is especially a problem for propulsion systems with closely coupled oxidizer tank and combustion chamber. For such systems, at the end of the liquid burn, the hot injector or back flow of hot gases could locally ignite the nitrous oxide vapor and start a deflagration wave that would freely propagate in the tank. The schematic of the flame propagation process in the oxidizer tank, which is the basis of our modeling approach, is illustrated in Figure 1. As shown in the figure we assume that the nitrous vapor in the tank is locally ignited at the injector end of the tank. Note that ignition at the forward end of the tank, which is less likely, would produce identical results.

Here we summarize the results of our model that is used to predict the pressure increase in a nitrous tank induced by the propagation of a deflagration wave (flame). The following are the assumptions implemented for this particular example case:

- No deflagration to detonation transition is allowed.
- No fast transient events have been included in the modeling.
- Ignition source is small enough such that the deflagration speed is close to the turbulent flame speed.
- The simplified first order kinetic model has been used.
- No heat transfer to the vessel walls.
- No liquid N_2O exists in the tank
- Initial composition is pure N_2O

Note that some of these assumptions are relaxed in the full version of the model. The simulated case has the following parameters.

- Initial temperature: 285 K
- Initial pressure: 42 atm (618 psi). Saturated vapor.
- Tank length: 2 m (78.7 inches)
- Tank L/D: 4

For this particular case the tank pressure and temperature are plotted as a function of time in Figures 13 and 14. The important data can be summarized as

- o Maximum pressure: 878 atm (12,900 psi)
- o Time to maximum pressure: 5.41 sec
- o Time to burst pressure 102 atm (1,500 psi): 2.0 sec
- o Maximum burned gas temperature: 3306 K
- o Minimum burned gas temperature: 1810 K
- o Maximum unburned gas temperature: 571.7 K

The temperature data for the burned gases as shown in Figure 13 indicates that, at the end of the decomposition process, the temperature distribution in the vessel is not uniform. In fact the ignition point has the hottest gases in the tank, since a burned gas element in this area of the tank gets compressed by the maximum possible pressure ratio. The unburned gases also get compressed. As shown in the figure, the

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extent of the temperature increase is somewhat limited (maximum unburned gas temperature less than 600 K), eliminating the possibility of secondary ignition (i.e. no knocking).
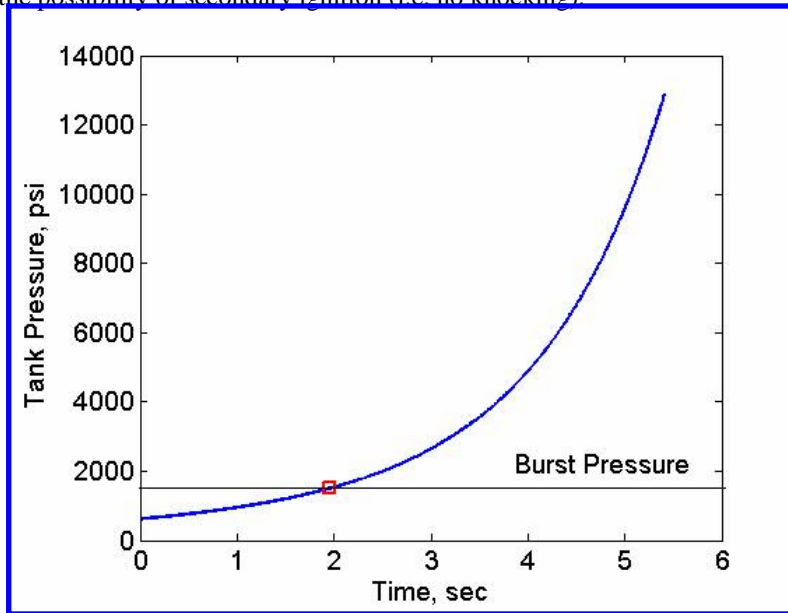

Figure 13: The pressure increase in the closed vessel as a function of time.

As a first approximation, the ideal final pressure, P_{max}, can be calculated using the following relationship

$$\frac{P_{max}}{P_o} = \frac{T_{fave}}{T_o} \frac{n_p}{n_r} \frac{1}{\left[1 + x_{N2O}(z_{N2O} - 1)\right]} \tag{28}$$

Here T_{fave} is the average temperature in the tank at the end of the decomposition process, x_{N2O} is the mole fraction of nitrous oxide at the start of the process. Since T_{fave} is a function of the compression ratio, an iterative process is needed to determine the maximum pressure.
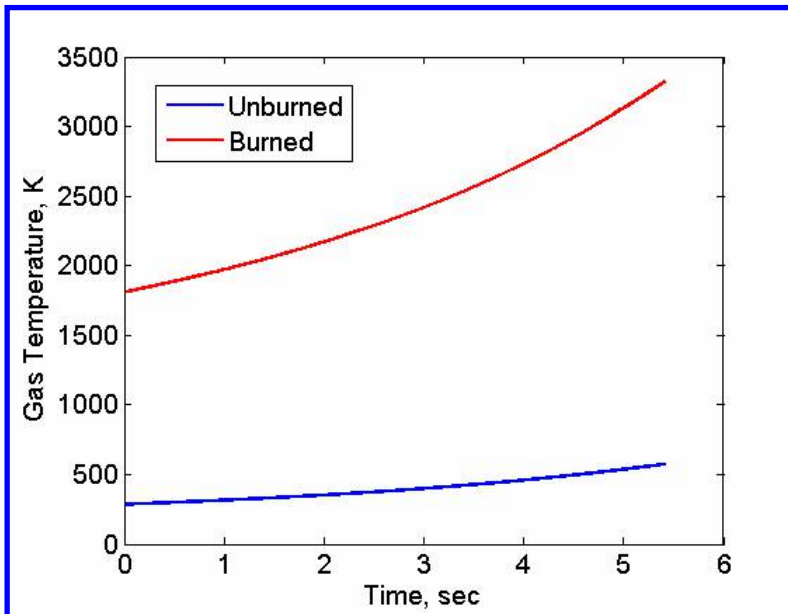
Figure 14: Temperature variation for the burned and unburned gases in the tank.

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Equation 28 has been used to estimate the ideal pressure ratio P_{max}/P_o as a function of oxygen mass fraction at three temperatures. The initial pressure is assumed to be the saturation value corresponding to the selected temperature. As shown in Figure 15, the ideal pressure ratio even at very high dilution levels is quite high, well above the safety factor of a flight vessel. This indicates that the real value of dilution is to reduce the ignitability of the mixture by increasing the minimum ignition energy, to increase the characteristic time for overpressurization by reducing the flame speed and finally to stretch the quenching distance. Note that the increase in the quenching distance and reduction in *dP/dt* elevates the relative importance of heat transfer which would lead to an actual pressure ratio smaller than the ideal value shown in Figure 15. As the initial temperature increases, the ideal pressure ratio also increases. This is a real gas effect and is driven by the compressibility of nitrous oxide.
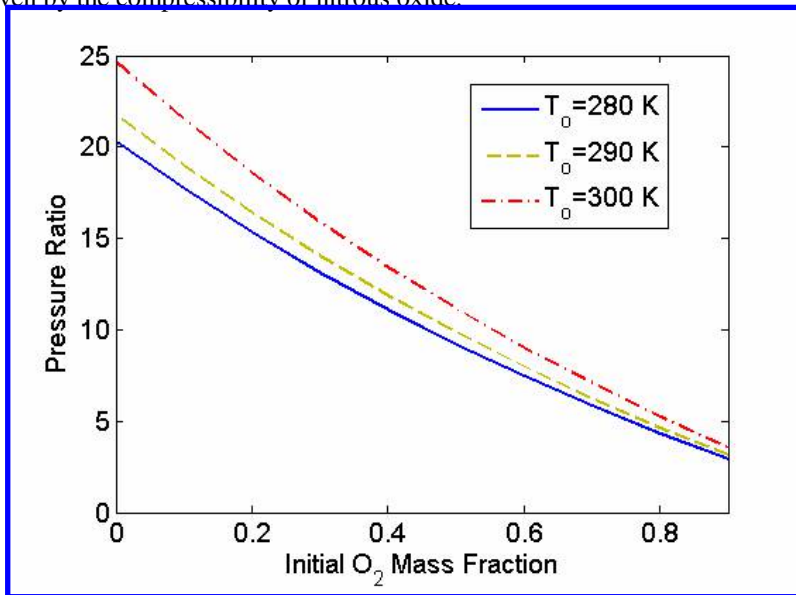

Figure 15: Pressure ratio P_{max}/P_o as a function of initial oxygen mass fraction for three initial temperatures

X) Conclusions and Safety Related Recommendations

The following conclusions can be drawn from the findings of this paper:

- Nitrous oxide is a widely used material with very interesting physical, chemical and biological properties. The number of serious chemical accidents reported for N_2O is quite limited considering the wide use of this material.
- The use of N_2O in propulsion applications presents unique hazards. This is mainly due to 1) the high temperature storage of N_2O in very large quantities (in run tanks and flight tanks), 2) large flow volume and high flow velocities and 3) the abundance of ignition sources in chemical propulsion systems. Thus the relative safety enjoyed in other applications should **not** be used as a guideline for safe operation.
- The relative safety of nitrous oxide compared to the other energetic propellants such as H_2O_2 is due to its slow kinetics which is partly caused by the "abnormal" nature of the decomposition step of the reaction which is governed by a spin-forbidden process.
- Using the findings in the literature, a detailed kinetics model has been established. It is well known that at pressures higher than 40 atm, the reaction rate reduces to first order. At high pressures relevant to propulsion applications, a simplified one step first order kinetics model is recommended.
- Models for homogenous and local thermal ignition have been developed. Local thermal ignition has been identified as the more feasible ignition mode for propulsion systems. It has been shown that the diluents significantly increase the minimum ignition energy enhancing the safety of the system significantly.

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- Local thermal ignition of the vapor in the tank ullage is arguably the greatest hazard that exists in an N_2O based propulsion system. The deflagration wave induced overpressurization in the tank has been demonstrated using an imaginary example case. Propulsion systems that have closely coupled oxidizer tanks and combustion chambers are believed to be particularly vulnerable to this mode of catastrophic failure.

The following are the safety related recommendations for N_2O based propulsion systems.

- Nitrous oxide is an energetic material and it must be respected! When N_2O is used in any risky testing or other operations, all personnel should be at a safe distance and/or in a protected area. A comprehensive hazard analysis is recommended, especially for large scale operations and testing.
- In manned systems, a properly designed pressure relief system must be installed on the flight tank. This system should be tested at full scale.
- The dilution of N_2O in the tank ullage by supercharging is highly recommended. Blow down N_2O systems, especially the ones that are allowed to burn in the vapor phase are inherently hazardous. Some of the possible diluents that can be used with N_2O systems are helium, molecular nitrogen and molecular oxygen.
- For small scale motor testing, the oxidizer tanks should be run in the vertical configuration such that a liquid layer of N_2O always separates the vapor in the tank ullage from the combustion chamber.
- In order to prevent accumulation of N_2O in the combustion chamber, the N_2O flow should always lag the igniter action.
- One should follow strict oxygen cleaning procedures for N_2O. Note that very small concentrations of fuels in N_2O might change the entire decomposition dynamics, making most of the findings with uncontaminated N_2O irrelevant[41]. Also note that the lean flammability limit for N_2O is zero, resulting in high sensitivity at very low concentrations of fuel.
- Nitrous oxide is a reasonably effective solvent for a number of hydrocarbons including a lot of common polymers. Any polymeric or nonpolymeric materials that will be used in the N_2O system should be carefully tested for compatibility. This includes the valve seals, o-rings or gaskets.
- One should avoid using catalytic materials in N_2O systems. A comprehensive list of catalytic materials for N_2O are given in Refs. 6 and 7.
- All past experience indicates that it is impossible to ignite and sustain a decomposition wave (detonation or deflagration) in liquid N_2O[4 and 31]. Note that fuel contamination in the liquid changes this situation, potentially resulting in very dangerous conditions.
- One must understand that it is almost impossible to eliminate all of the ignition sources in a practical system. A system should be designed to mitigate a potential decomposition event. The famous quote by Trevor Kletz is worth remembering in the design and operation of N_2O based propulsion systems[41].

"Ignition source is always free"

Despite its decomposition hazard, nitrous oxide is still a much safer material compared to the other monopropellants used in the industry including H_2O_2. In our opinion, if handled properly, nitrous oxide (or other N_2O containing oxidizers) is one of the safest oxidizers used in chemical propulsion systems.

XI) Acknowledgements

XII) References

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Appendix - Physical Properties of Nitrous Oxide

Due to the proximity of its critical temperature with the locus of typical application temperatures, it behaves very non-ideally in both the gas and liquid phases at standard temperatures (where the reduced temperature, $T_r = T/T_c$, > .95). The strong non-ideality makes modeling and measurement more complex and demands the use of good thermo-physical property models. Figure A-1 depicts the *T-s* cross section of the property space for nitrous oxide.
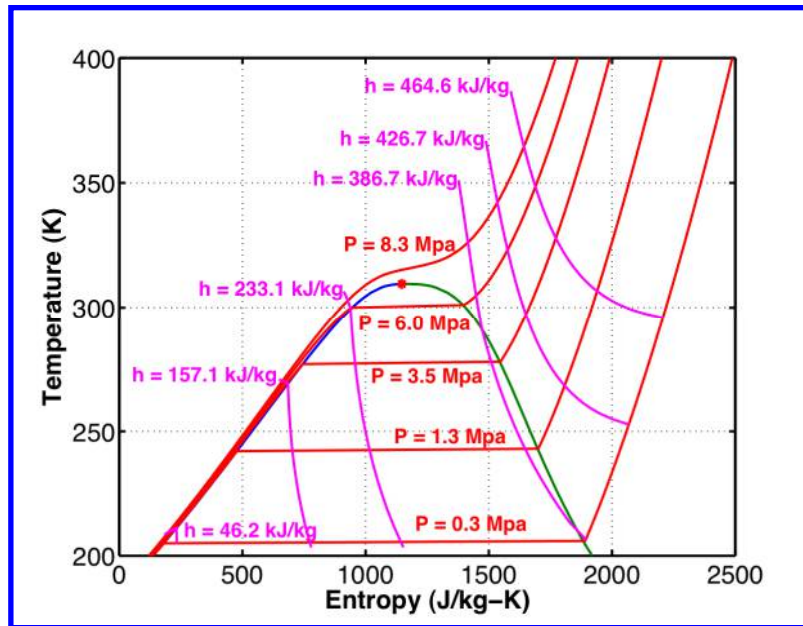
Figure A-1: *T-s* diagram for nitrous oxide.

Nitrous oxide has a very narrow liquid temperature range at atmospheric pressure, freezing at 182.29 K and boiling at 184.67K. For this reason it is generally used at pressures significantly above atmospheric where its saturation temperature is near its critical point. Table A-1 lists several commonly used propellants and their compressibilities in the liquid and vapor phase at conditions where they are typically used. Notice that as the critical temperature gets closer to the operating temperature, the compressibilities differ significantly from ideal. For this reason, the ideal gas law gives grossly inaccurate results for the vapor phase and the constant density assumption breaks down in the liquid phase.

The phase behavior of nitrous oxide is also important as it is typically used at or near its saturated state. In order to predict both physical properties and phase equilibrium, a good equation of state is necessary. For many purposes the Peng-Robinson[36] cubic equation of state does a good job of predicting phase behavior and physical properties of nitrous oxide although it tends to become inaccurate in the liquid phase near the critical point. For higher accuracy at the cost of complexity, a multi-parameter equation of state such as the Span-Wagner Fundamental Equation of State[42] can be used.

Table A-1: Critical temperatures and compressibility factors for fluids often used as propellants. Liquid oxygen and Liquid hydrogen saturated at 1 atm, others at 298K.

Fluid	Critical Temperature	Liquid Compressibility	Vapor Compressibility
Water (H_2O)	647.0 K	2.3×10^{-6}	0.997
Decane ($C_{10}H_{22}$)	617.7 K	1.4×10^{-6}	0.994
Liquid Oxygen (O_2) [90K]	154.6 K	0.004	0.97
Liquid Hydrogen (H_2) [20K]	33.2 K	0.017	0.90
Propane (C_3H_8)	370.0 K	0.034	0.82
Nitrous Oxide (N_2O)	309.5 K	0.13	0.53

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