AA 284a
Advanced Rocket Propulsion

Lecture 5
Thermochemistry and Propellants
Part 2

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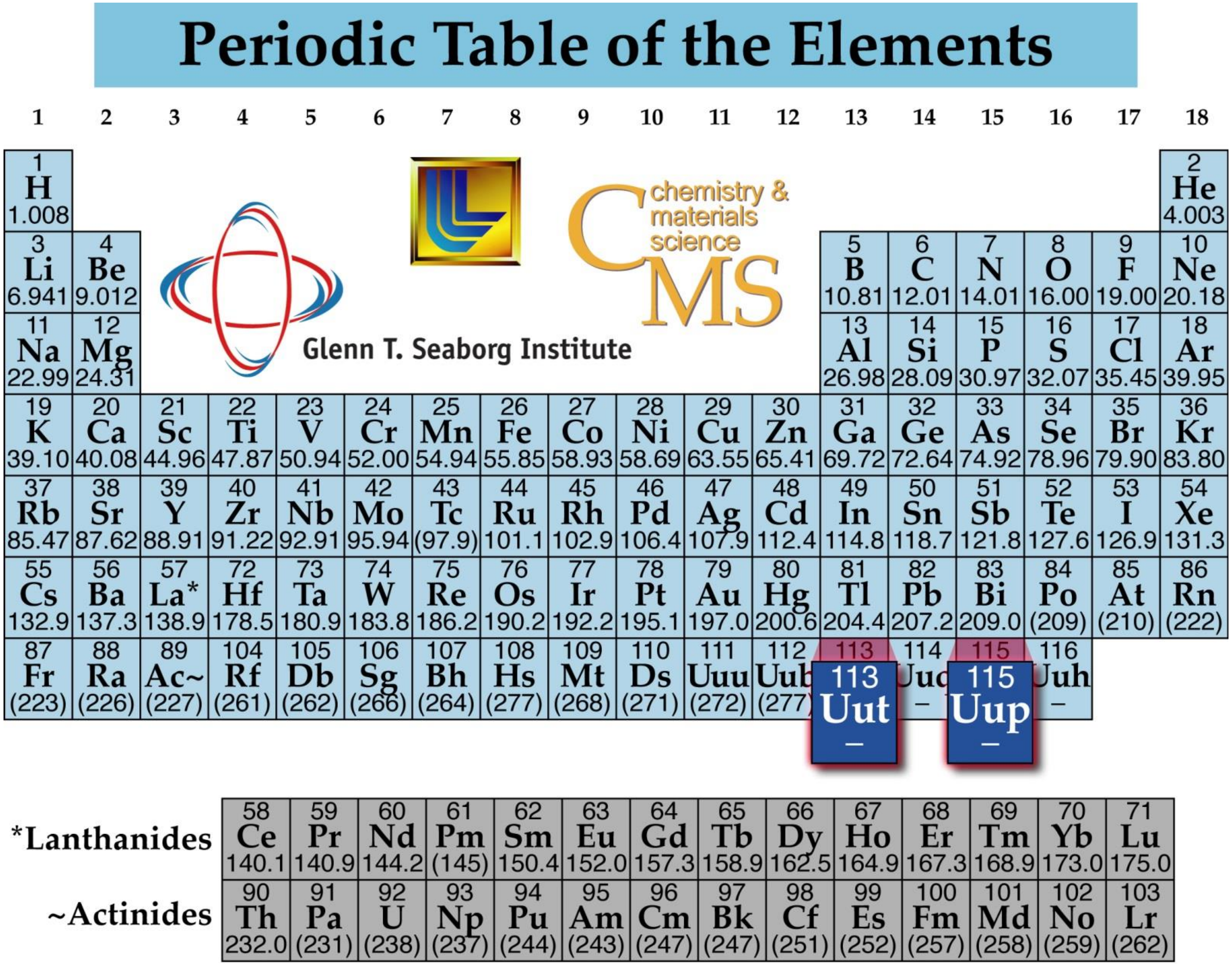
Key Properties of Propellants

- Isp Performance: Minimize mass
- Density or Impulse Density (Isp*density): Minimize volume
- Physical state in storage at storage temperature
  - Gas, liquid, solid --> Classification of chemical rockets: liquid, solid, hybrid
  - Storability aspect: Cryogenic: LOX, Earth Storable: H_2O_2, N_2O_4
  - Vapor pressure at operational temperatures:
    - Self pressurized (N_2O)
    - Ullage pressure for pump fed systems
- Chemical Kinetics
  - Motor stability
  - Efficiency
  - Ignition characteristics: Hypergolic behavior (N_2O_4-N_2H_4)

Key Properties of Propellants

- Toxicity: acute, chronic, carcinogenic
- Stability: Resistance to self decomposition
  - Slow process: loss of energy in time
    - H2O2 decomposes slowly
    - Phase stability of AN
  - Fast process (explosions/detonations): safety
- Corrosion Characteristics
  - Nitric acid, IRFNA
  - Inhibitors (HF)
- Environmental Issues (Example: Chlorines)
- Cost

Propellant Formulation



Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.9)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Uuu (272)	112 Uub (277)	113 Uut –	114 Uuq –	115 Uup –	116 Uuh –		

*Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
~Actinides	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Propellants – Light Elements as Fuels

- Consider the performance of the elements (in their most common allotropic form) with molecular oxygen as the oxidizer

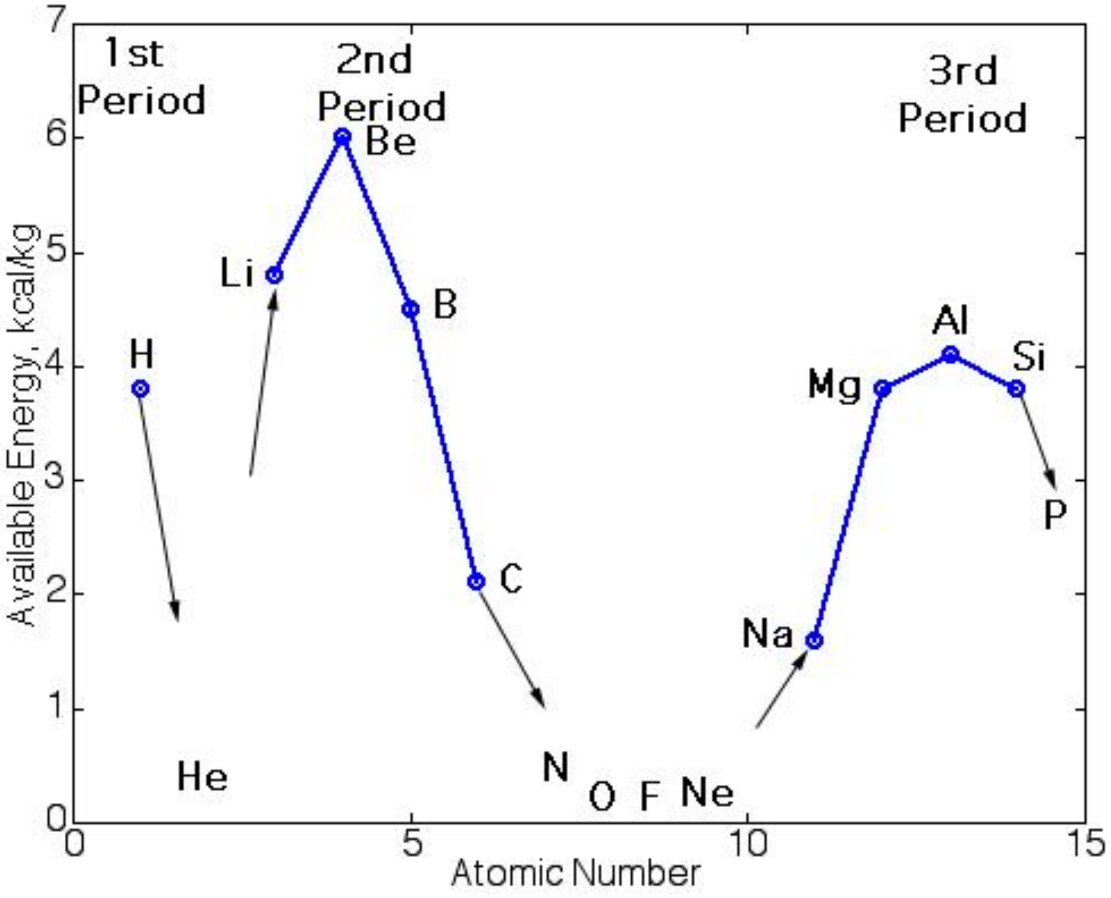
$$\frac{n}{k}X_k + \frac{m}{2}O_2 \rightarrow X_nO_m$$

- The chemical structure of the primary combustion product can be determined based on the Lewis structure and the Octet rule
  - Example: Al2O3, BeO, MgO, Li2O
- Assume that the combustion is at the stoichiometric O/F and the dissociated products are excluded
- The reactants and products are assumed to be at 25 C and at their states that they typically exist at this particular temperature
  - Example:
    - Al: Al2O3 in solid phase
    - H: H2O2 in liquid phase
    - C: CO2 in gaseous phase
- Note that the heat of reaction is equal to the heat of formation of the end product

Propellants – Light Elements as Fuels

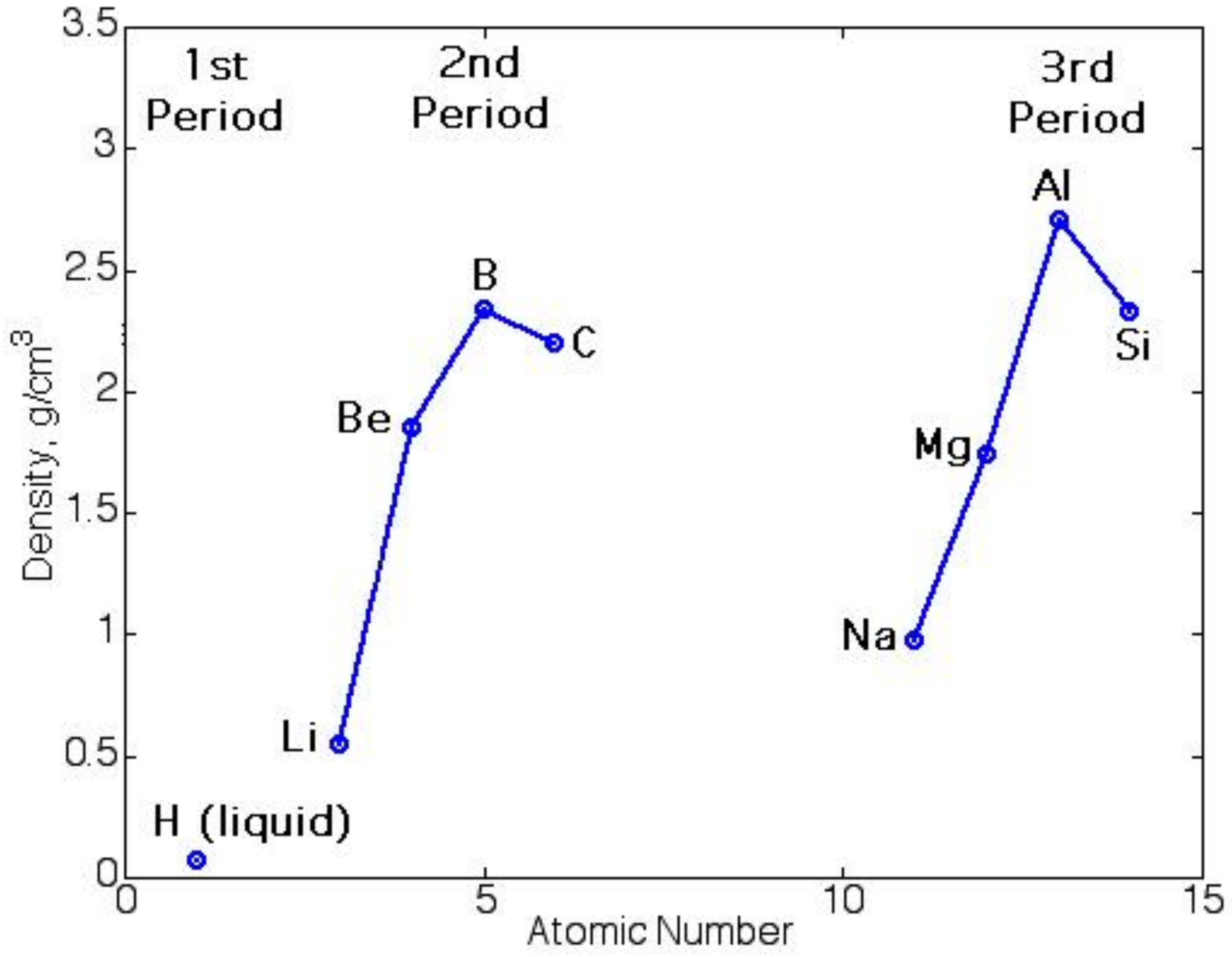
Element	Product (phase)	MW of Product (g/mole)	Heat of Formation @ 25 C (kcal/mole)	Combustion Energy (kcal/g)
Al	Al2O3 (c)	102	-399.1	3.91
B	B2O3 (c)	70	-305.4	4.35
H	H2O (c)	18	-68.3	3.75
C	CO2 (g)	44	-94.1	2.14
Li	Li2O (c)	30	-144.0	4.80
Mg	MgO (c)	40	-143.8	3.60
Be	BeO (c)	25	-146.0	5.84

Propellants – Available Heat of Reaction for light elements with O2 at Stoichiometric Mixture



- In order to maximize the available energy
  - Have strong bonds (in the products)
  - Have light elements (also helps c* and Isp)
- Generally available heat correlates well with the adiabatic flame temperature
- Be is the most energetic element
- Al is the most energetic practical element

Density of Light Elements - Most common Allotrope @ 298 K



Propellants – Effect of Dissociation

- Consider the combustion of H2 with two high energy oxidizers, F2 and O2
  - Oxygen:
    - Available Energy: 3.60 kcal/g
    - Adiabatic Flame Temperature: 2760 K (O/F=2.27)
    - MWp: 9.0 g/mol
    - Isp=350 sec (Pc/Pe=20)

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

  - Fluorine:
    - Available Energy: 3.11 kcal/g
    - Adiabatic Flame Temperature: 3323 K (O/F=3.33)
    - MWp: 10.0 g/mol
    - Isp=364 sec (Pc/Pe=20)

$$\frac{1}{2}H_2 + \frac{1}{2}F_2 \rightarrow HF$$

- Reduced Isp is due to the dissociation of the products.
  - HF is more resistant to dissociation compared to H2O
- Resistance to dissociation of various molecules at 2500 K and 20 atm can be ranked as
  - N2 > CO > HF > BF3 > Al2O3 > B2O3 > H2O > CO2
  - Generally molecules containing O dissociate more easily compared to molecules containing F. This partially explains the superior performance of F2 compared to O2

Propellants – Oxidizers

- All elements with strong oxidizing capability are positioned in the upper right section of the periodic table (Many of them are halogens)
- All oxidizers that are composed of single element are liquids or gases under ambient conditions
- Here is a list of oxidizers that has been considered or used in the rocket propulsion applications
- Oxygen (O_2):
  - Most abundant element in the crust of earth (50% by mass including the oceans and the atmosphere)
  - Most widely used oxidizer in liquid propulsion (and possibly in the hybrid propulsion)
  - Best performing (Isp) practical oxidizer
  - Extremely low boiling point 90 K (Cryogenic)
  - Readily available, very inexpensive, obtained by liquefaction and fractioning of air
  - Modest specific density: 1.14
- Ozone (O_3): (Not Used)
  - Excellent performance (as good as F_2)
  - Very unstable in large concentration (liquid O_3 is shock sensitive), Highly toxic
  - Typically mixed with O_2 at varying concentrations

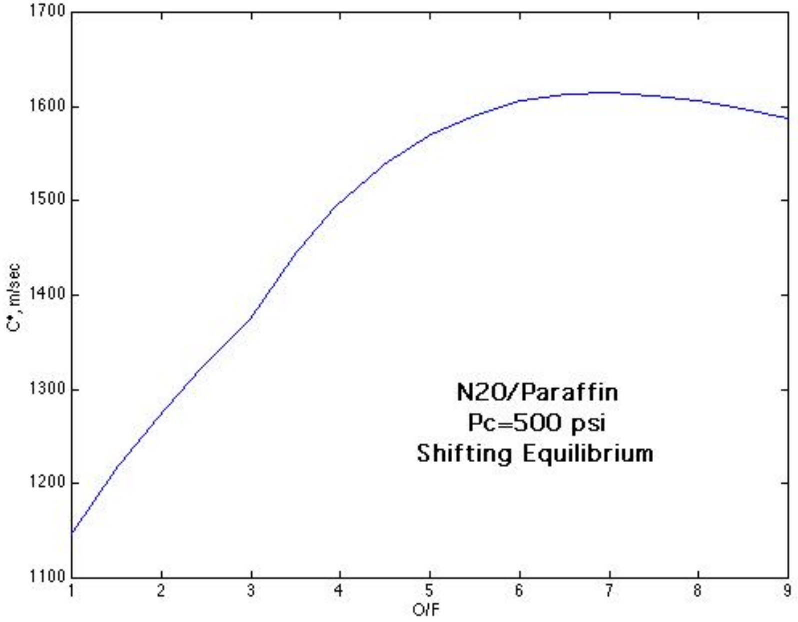
Propellants – Oxidizers

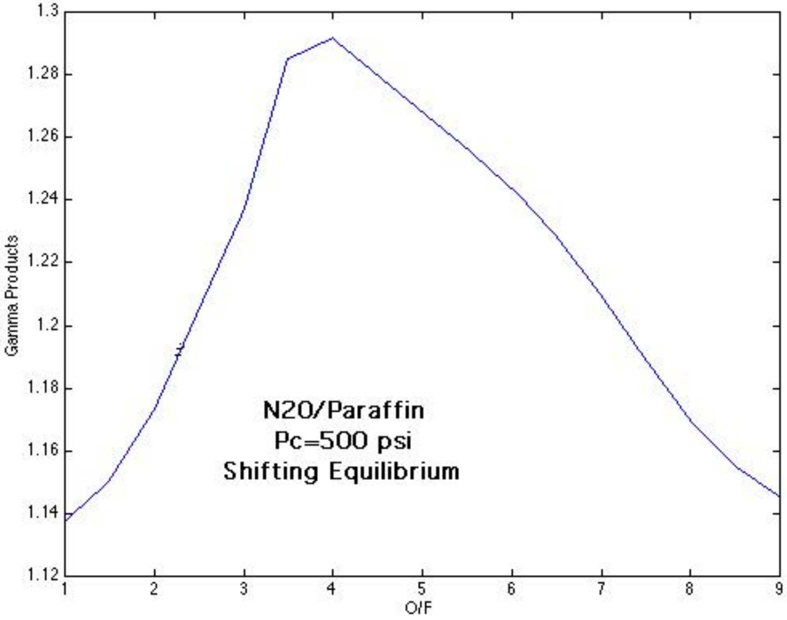
- Fluorine (F2): (Not Used)
  - Highest oxidizing power among all the elements (largest electronegativity)
  - Extremely reactive (very difficult to handle)
  - Best performing oxidizing agent in terms of Isp with most fuels
    - High energy content, low MW products (limited dissociation compared to O2)
    - With carbon containing fuels, Isp is lowered due to heavy CF4 formation
    - Mixed with O2 at various concentrations to minimize the CF4 formation (FLOX)
  - Cryogenic- Low boiling point 85.24 K, yellow colored liquid in condensed phase
  - Denser than O2: 1.56 (specific gravity)
  - Hypergolic with all fuels
  - Acutely toxic
  - Can be stored in metal tanks (Nickel, Monel, Aluminum, some stainless steel)
    - Fluorine oxide layer protects the metal
- Fluorine Compounds: (Not Used)
  - Chlorine Trifluoride (ClF3), Perchloryl Fluoride (ClO3F)
  - NOF, NO2F, NF3, F2O
- Chlorine Oxides: (Not Used)
  - Cl2O, ClO2, Cl2O6, Cl2O7
  - All unstable

Propellants – Oxidizers

- Nitrogen Oxides:
- Nitrous Oxide (N2O): (Used)
    - Resonant molecular structure, positive heat of formation, can be used as a monopropellant, decomposition reaction is exothermic, unexplored safety issues for large masses
    - Used as anesthetic in dentistry. Also used in the semiconductor industry
    - Advantages
        - Widely available, reasonably inexpensive
        - Only toxic in high concentrations
        - Self pressurizing capability (see Lecture 3 notes for P-T and rho-T diagrams)
    - Commonly used in the hybrid rocket propulsion systems (systems with low Delta V requirements)
        - SpaceShipOne, SpaceShipTwo
        - Space Dev launch vehicle
        - Hobby rockets
        - Educational sounding rockets
    - Shortcomings
        - Low to medium Isp (low oxygen mass in the molecule), low density
        - Decomposition hazard
        - Strong dependence of density and pressure on temperature (critical temperature 36.5 C)

C* and Gamma for the N2O/Paraffin System





Propellants – Oxidizers

- Nitrogen Oxides:
- Nitric Oxide (NO): (Not Used)
  - Very high vapor pressure (critical temperature -93.0 C) – gas under ambient conditions
  - Used in the mixtures of nitrogen oxides
- Nitrogen Tetroxide (N2O4): (Used)
  - Liquid with relatively low vapor pressure (14 psi at 20 C)
  - Cannot be used as a self pressurizing system
  - Strong oxidizer compared to the other nitrogen oxidizes (high oxygen mass fraction in the molecule)
  - Widely used in the US systems in the past and current being used in a lot of the international systems
  - Toxic
- Nitrogen Dioxide (NO2):
  - In chemical equilibrium with the N2O4

$$2NO_2 \leftrightarrow N_2O_4$$

  - At low temperatures N2O4 is the high concentration component.

Propellants – Oxidizers

- Hydrogen Oxides:
- Hydrogen Peroxide (H2O2): (Used)
  - Can be used as fuel, oxidizer and monopropellant
  - Used in ME 163 as the oxidizer, used in the 50-60’s. Recently became popular again
  - Colorless liquid, slightly unstable, completely miscible in water, used at different concentrations with water (70-98% H2O2)
  - Not completely storable:
    - Slow decomposition: 1-3 % a year (depends on the purity level in storage tank etc…)
    - Storage in pure aluminum tanks is relatively safe
  - Toxicity: Irritates skin
  - High density oxidizer: 1.45 (specific density)
  - Hypergolic with certain fuels
  - Can be used with a catalyst bed with the non-hypergolic fuels. (Silver, permanganetes are common catalysts)

$$H_2O_2 \xrightarrow{13\ kcal/mole} H_2O + \frac{1}{2}O_2$$

  - Moderate Isp
  - Potential stability/shock sensitivity problem especially in large quantities
- Water (H2O):
  - Low Isp
  - Extremely abundant and inexpensive and also very easy to handle

Propellants – Oxidizers

- Nitric Acid (HNO3): (Used)
  - Widely used as an oxidizer (Especially internationally)
  - Anhydrous Nitric Acid: (> 99.0% HNO3)
  - White Fuming Nitric Acid (WFNA): (97.5 % HNO3, 2 % H2O, 0-0.5 % N2O4)
  - Red Fuming Nitric Acid (RFNA): (82-85 % HNO3, 2-3 % H2O, 13-15 % N2O4)
    - Inhibited Red Fuming Nitric Acid (IRFNA): 0.4-0.6 % HF is added to inhibit the corrosive effects of nitric acid
    - Gellified Inhibited Red Fuming Nitric Acid (GIRFNA): Add some gellifying agents to IRFNA
  - Storable - Liquid with low vapor pressure (0.93 psi @ 20 C)
  - Corrosion is an issue but stability is not
  - Aluminum or stainless steel are good tank materials
  - Moderate Isp performance (low compared to N2O4)
  - High Density: 1.52 (specific density) – best of the storable oxidizers
  - Low freezing point (-41.6 C)

Properties of Liquid Oxidizers

Oxidizer	Formula	Isp Capability	Density, g/cm^3 (Temp K)	Boiling Temp, K	Melting Point, K	Corrosion	Toxicity	Shock Sensitivity
Oxygen	O2	High	1.14 (91.2)	90.2	54.4	None	None	Insensitive
Nitrous Oxide	N2O	Moderate	0.75 (298)			None	None	Insensitive
Nitrogen Tetraoxide	N2O4	Mod/High	1.45 (293)	294.2	261.9	Corrosive	Very Toxic	Insensitive
Hydrogen Peroxide (> 90%)	H2O2	Moderate	1.448 (293)	423.7	273.5	Very corrosive	Causes burns	Sensitive
Nitric Acid	HNO3	Moderate	1.52 (283)	359	231.5	Very corrosive	Very Toxic	Insensitive
Exotic Oxidizers								
Fluorine	F2	Very High	1.54 (77.2)	85.24	55.2	Corrosive	Very Toxic	Insensitive
Ozone	O3	Very High	1.571(90)	162.7	89	None	Very Toxic	Very sensitive
Oxygen bifluoride	F2O	Very High	1.65 (286)	128.36	49.36	None	Toxic	Insensitive

Propellants – Oxidizers

- Solid Oxidizers
- Typically low energy oxidizers due to reduced mass fraction of oxidizer in the molecule
- Perchlorates:
  - Metal-ClO4
- Amonium Perchlorate (NH_4ClO_4) (AP): (Used)
  - White crystals
  - Explosive at high temperatures
  - Widely used in the modern solid propellant rockets
  - Specific density: 1.95
  - Moderate Isp (mass fraction of the oxidizing agents in the molecule)
  - Exhaust gases are highly corrosive and toxic (HCl acid)
- Lithium Perchlorate ($LiClO_4$): (Not Used)
  - Hygroscopic-limits the usage
- Potassium Perchlorate ($KClO_4$): (Limited Usage)
  - More stable than AP
  - Higher density: 2.52 (specific density)
  - Lower Isp compared to AP (Heavier MW products)

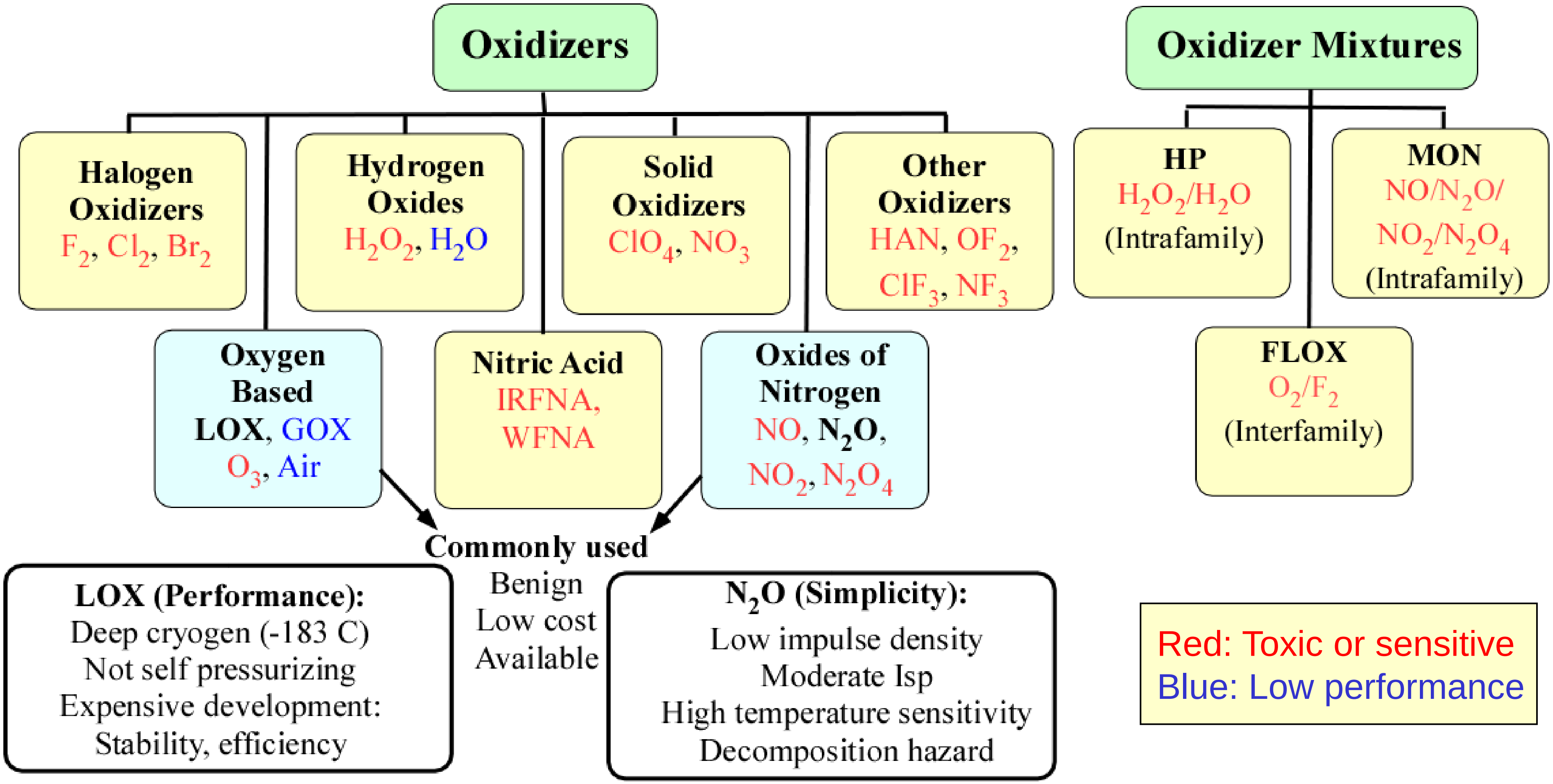
Propellants – Oxidizers

- Inorganic Nitrates
  - Metal-NO3
- Amonium Nitrate (NH4NO3) (AN): (Used)
  - White crystals
  - Used as fertilizers
  - Extremely flammable and explosive
  - Low Isp compared to AP
  - Specific density: 1.73
  - Not used widely in the solid rocket industry
  - Advantages: available, inexpensive, smokeless exhaust, nontoxic combustion products
  - Solid to solid phase chance at temperatures higher than 30 C resulting in a 8 % volume change. Results in cracking
  - Phase stabilized version of AN is available
- Potassium Nitrate (KNO3): (Limited Use)
  - Used in matches and fertilizers
  - Transparent crystalline powder
  - Performance is lower than AN (specific density: 2.109)

Properties of Solid Oxidizers

Oxidizer	Formula	Oxygen Content (% mass)	Density, g/cm^3	Heat of Formation, kcal/mol	Products of Combustion	Isp Performance
Ammonium perclorate	NH4ClO4	54.5	1.949	-69.42	N2, HCl, H2O	Medium
Ammonium nitrate	NH4NO3	60.0	1.730	-87.27	N2, H2O	Medium
Potassium perclorate	KClO4	46.2	2.519	-103.6	KCl	Medium
Potassium nitrate	KNO3	47.2	2.109	-117.76	K2O	Low

Oxidizers Overall Picture



Oxidizers

Halogen Oxidizers
F_2, Cl_2, Br_2

Hydrogen Oxides
H_2O_2, H_2O

Solid Oxidizers
ClO_4, NO_3

Other Oxidizers
HAN, OF_2, ClF_3, NF_3

Oxygen Based
LOX, GOX
O_3, Air

Nitric Acid
IRFNA, WFNA

Oxides of Nitrogen
NO, **N_2O**, NO_2, N_2O_4

Oxidizer Mixtures

HP
H_2O_2/H_2O
(Intrafamily)

MON
$NO/N_2O/NO_2/N_2O_4$
(Intrafamily)

FLOX
O_2/F_2
(Interfamily)

Commonly used
Benign
Low cost
Available

LOX (Performance):
Deep cryogen (-183 C)
Not self pressurizing
Expensive development:
Stability, efficiency

N_2O (Simplicity):
Low impulse density
Moderate Isp
High temperature sensitivity
Decomposition hazard

Red: Toxic or sensitive
Blue: Low performance

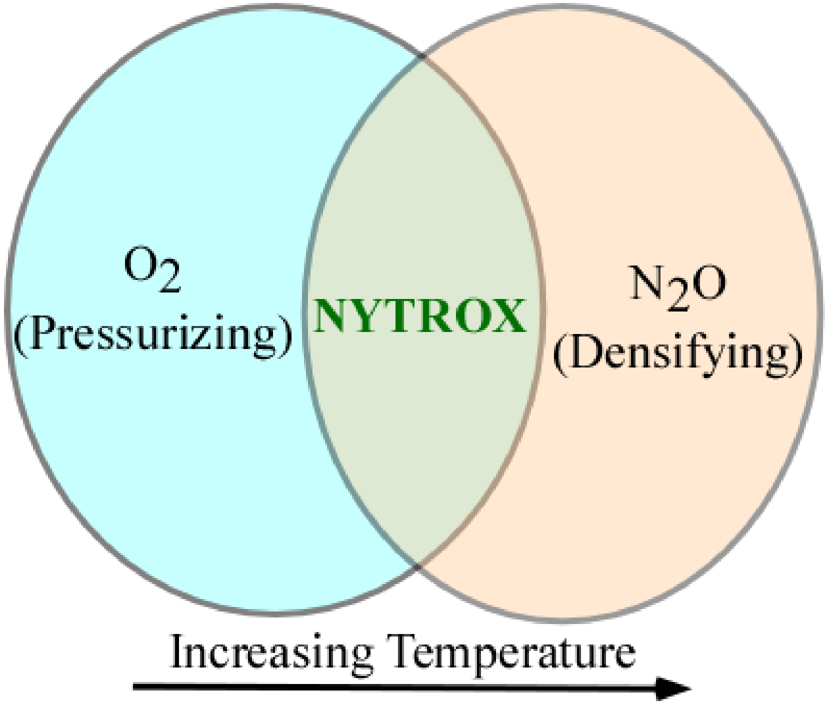
No perfect oxidizer exists to be used in chemical rocket propulsion applications

Nytrox* Opportunity

A new class of oxidizers with favorable properties can be formulated as equilibrium and non-equilibrium mixtures of N_2O and O_2.

N_2O is the densifing component and O_2 serves as the pressurant.

Nytrox has a number of advantages over the pure components.



Nytrox Variations: 1) Other oxides of nitrogen and 2) meta-stable mixtures

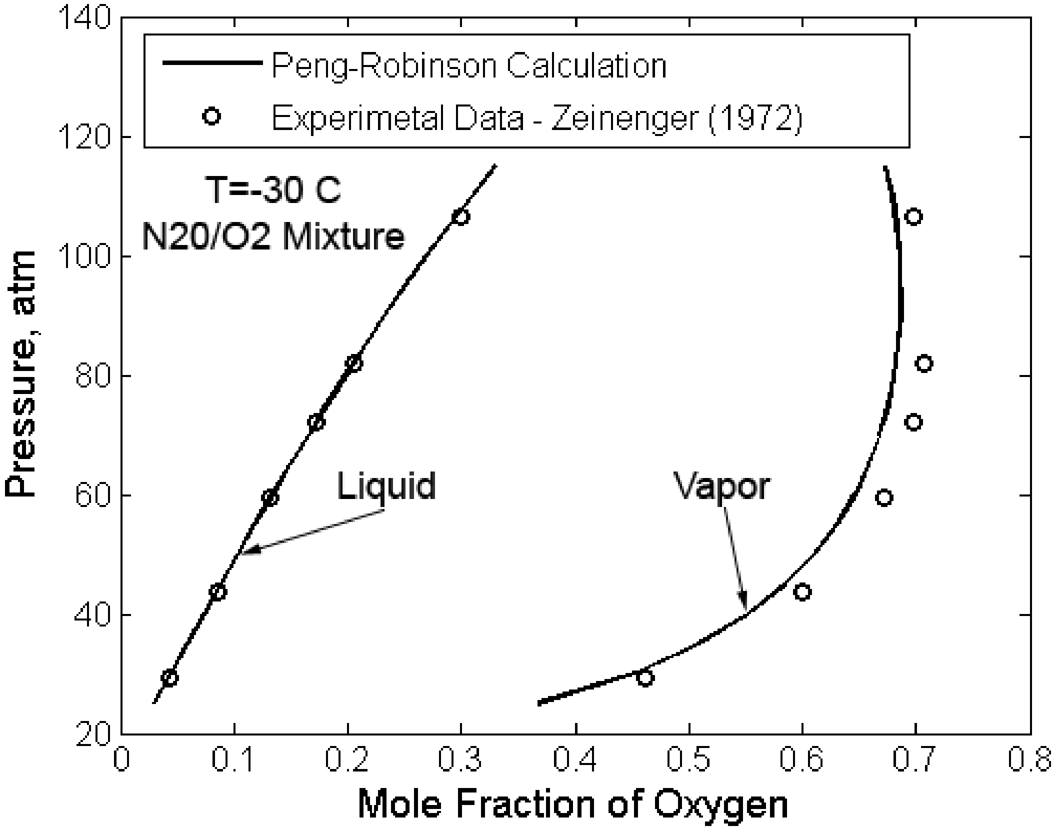
This mixture was never considered in the context of rocket propulsion

Patent pending: M. A. Karabeyoglu, “Mixtures of Oxygen and Oxides of Nitrogen as Oxidizers for Propulsion, Gas Generation and Power Generation Applications”, November 2007.

Nytrox Feasibility

Gas phase mixtures of N_2O and O_2 are commonly used in medical and dental applications as an anesthetic.

Equilibrium liquid/vapor mixtures of N_2O and O_2 have been studied to demonstrate safe storability at low temperatures.



Experimental data on the mixtures of N_2O/O_2 exists

Data shows that these substances are highly miscible

Nytrox Advantages

Compared to LOX and N_2O

Benign nature of the pure components is retained.

Self pressurization possible at high densities.

Optimization possible based on mission requirements.

Non-equilibrium mixtures can be used to improve the system performance significantly.

Efficient vapor phase combustion. Improved delivered Isp.

Compared to LOX

Not a deep cryogen. Oxidizer at -60 C or -40 C is much easier to manage. Composite tanks can be used. These temperatures are ideal for MAV.

Easier to develop stable and efficient motors

Safe operation due to reduced fire and cryogenic hazard

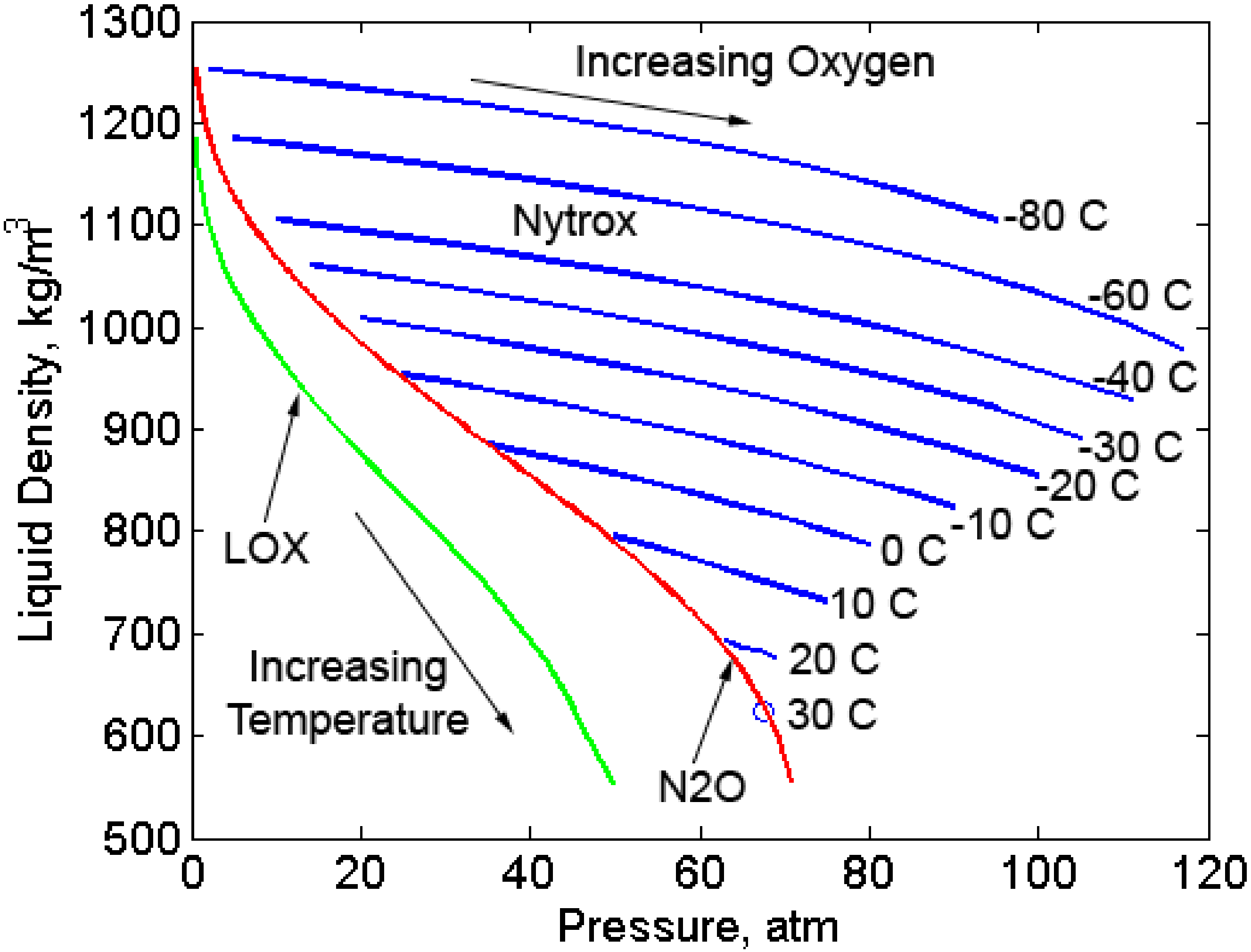
Compared to N_2O

Improved Isp performance.

Lower freezing point compared to N_2O (-90.8 C).

Safe compared to N_2O due to reduced decomposition hazard in the ullage and in the feed lines.

Nytrox Density vs. Pressure



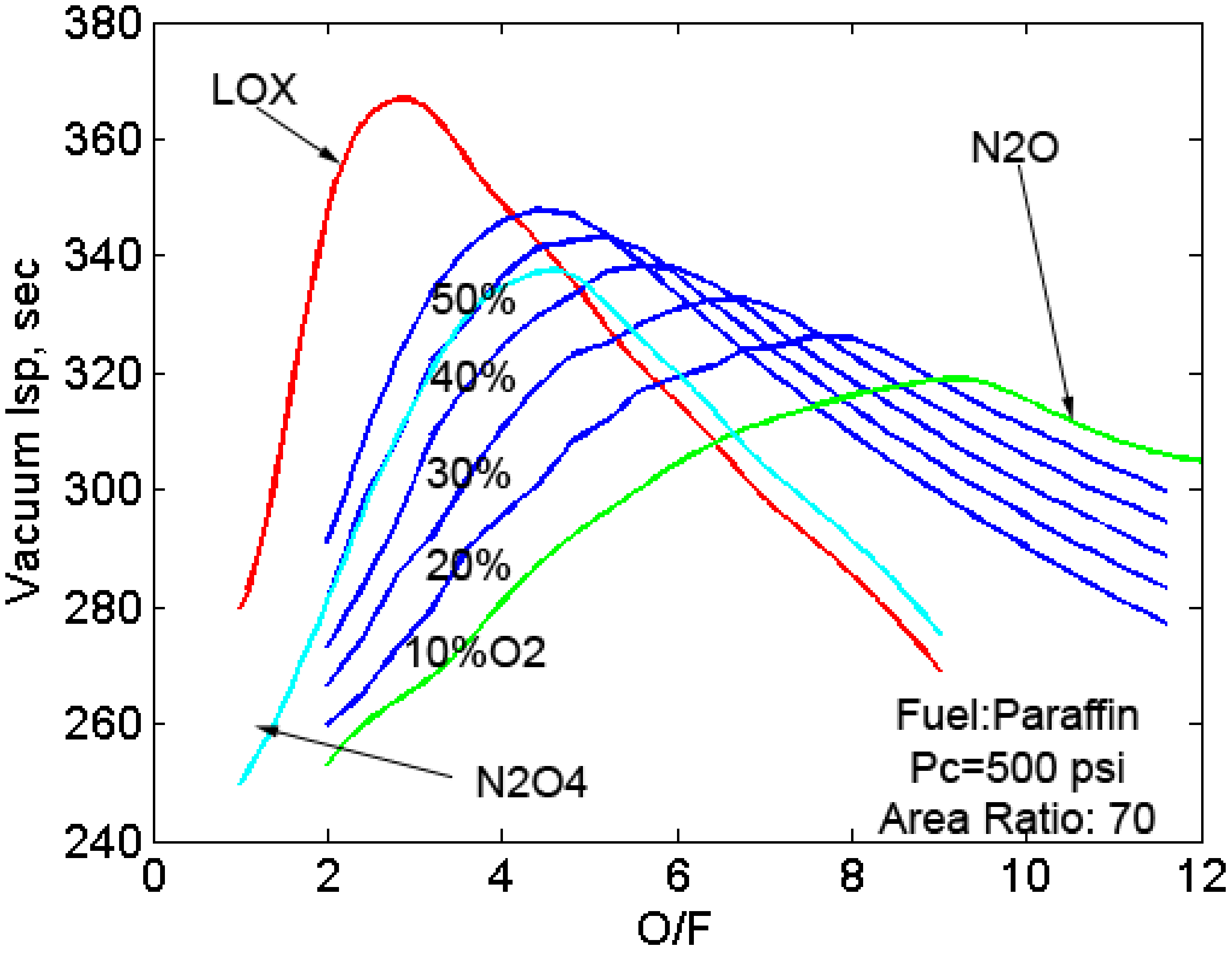
Self pressurization at high density

Reduced sensitivity

Cold liquid (Not cryogenic)

Large parameter space for optimization

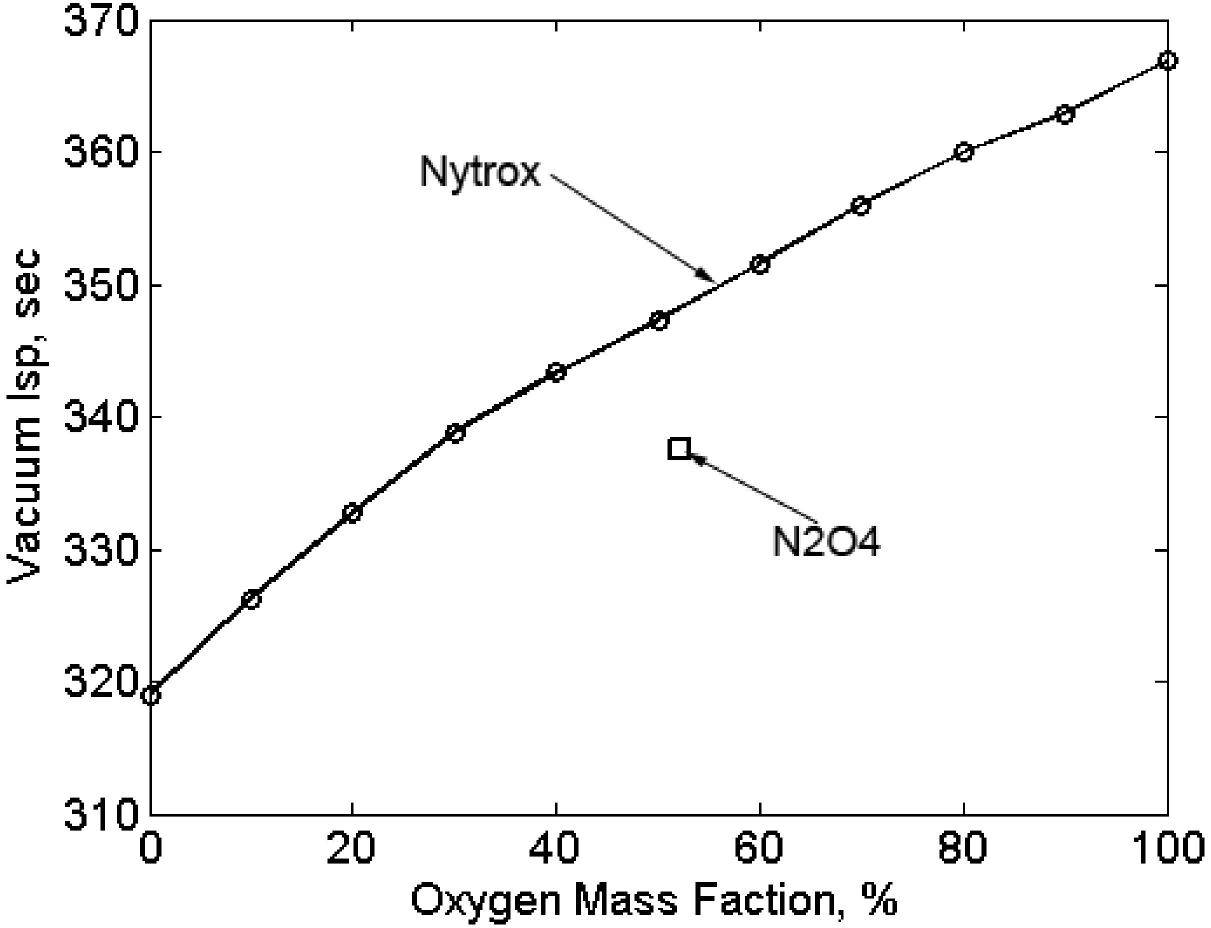
Nytrox Isp Performance



Improved Isp performance over N_2O

N_2O_4 performance is matched at ~30% O_2 concentration

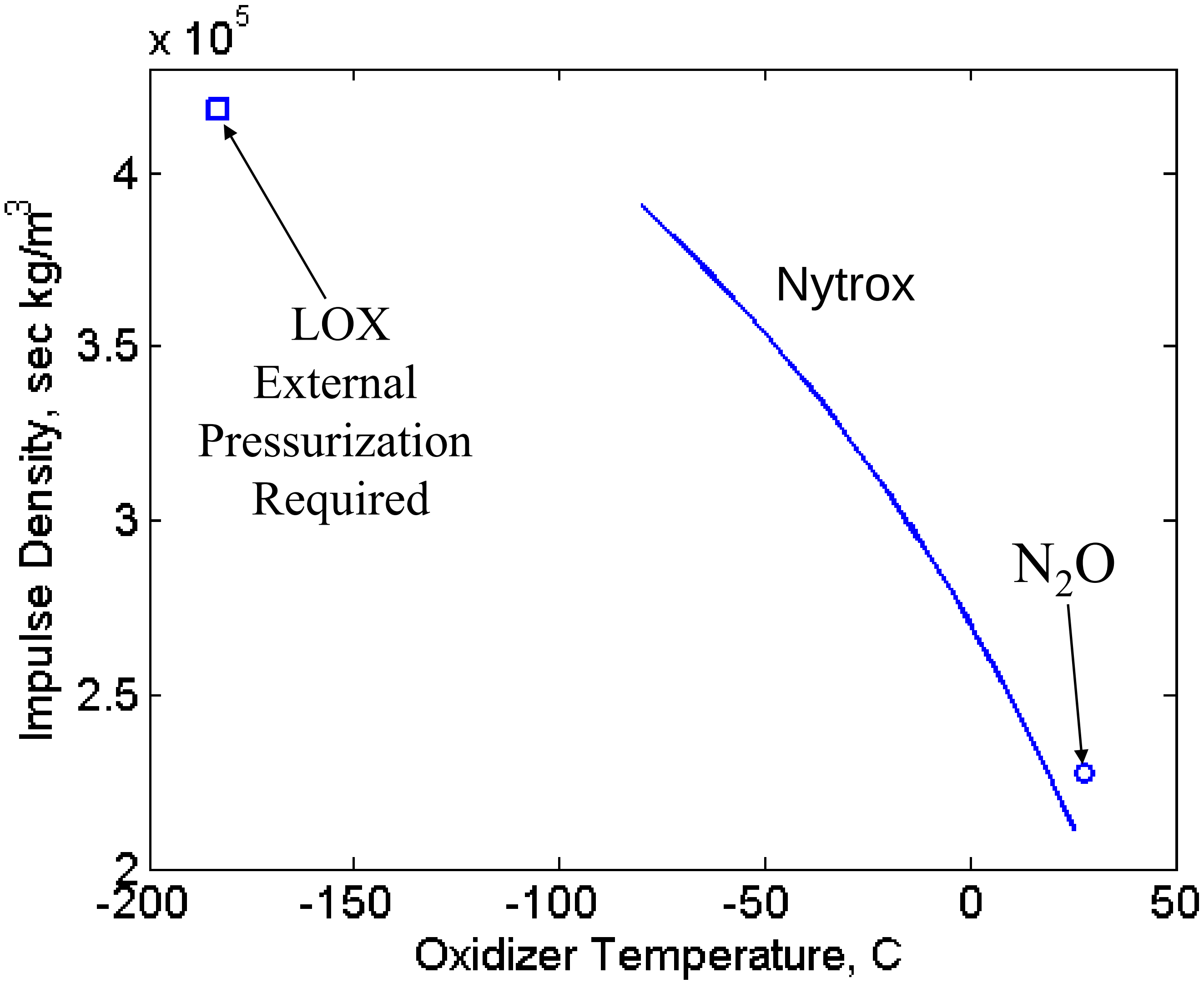
Nytrox Oxygen Fraction



Nytrox outperforms N_2O_4 at the corresponding oxygen mass fraction

~10 sec Isp improvement over N_2O at 15% O_2 level

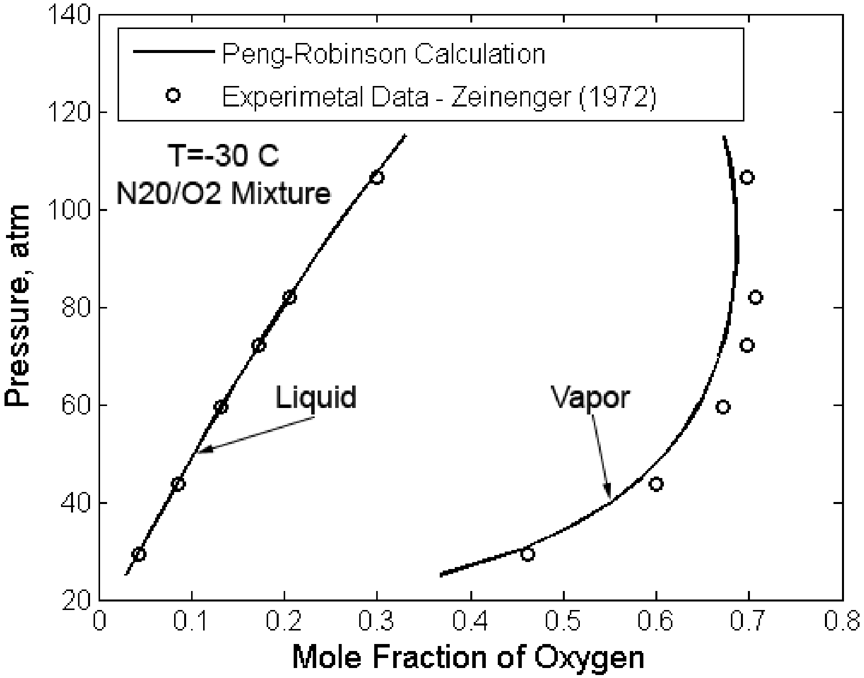
Nytrox Impulse Density vs. Temperature @ 60 atm



High impulse density with self-pressurization

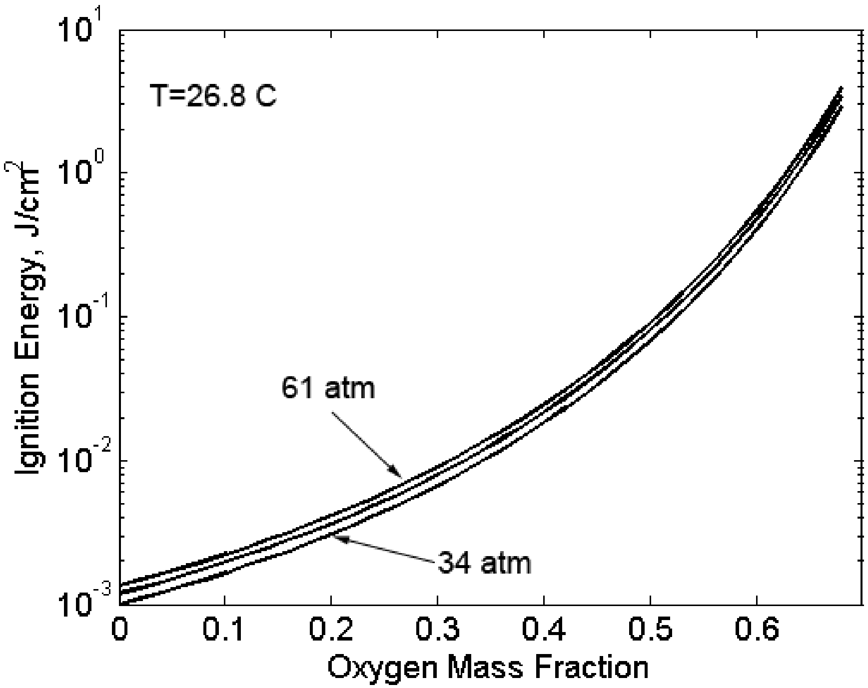
Nytrox Safety

Nytrox is safer compared to pure N_2O because of the dilution effect of oxygen in the vapor phase.



Vapor phase is primarily composed of oxygen

Ignition energy to start a deflagration wave for Nytrox is 1000 times larger



Propellants – Fuels

- Nitrogen Containing Fuels:
- Ammonia (NH_3):
  - Liquid, good Isp performance with various oxidizers
- Amines:
  - Organic derivatives of ammonia
  - Replace the hydrogen atom with organic radicals (example: methyl group)
  - Examples
    - Methylamine ($(CH_3)NH_2$): gas under ambient conditions
    - Dimethylamine ($(CH_3)_2NH$): gas under ambient conditions
    - Trimethylamine ($(CH_3)_3N$): liquid under ambient conditions
    - Aniline ($(C_6H_6)NH_2$): Replace hydrogen with a benzene ring, oily liquid (poison)
  - Amines are used as additives to the liquid propellants to enhance the combustion stability behavior of liquid engines
- Hydrazine (N_2H_4):
  - Also known as anhydrous hydrazine
  - Oily hygroscopic liquid
  - Hypergolic with halogens, liquid oxygen, H_2O_2 and N_2O_4
  - Mixes with water

Propellants – Fuels

        - High Isp performance (Superior to ammonia, amines, hydrocarbons with storable oxidizers, Secondary to hydrogen)
            - High hydrogen content
            - High energy content (positive heat of formation)
        - High liquid density: specific gravity of 1.009 at 20 C
        - Stable combustion (partly induced by the hypergolic nature)
        - Relatively high freezing point: 1.4 C

- Hydrazine Hydrate (NH2 NH2 H2O):
    - Lower Isp performance compared to hydrazine
    - Used in WWII by Germans
        - Hydrazine hydrate with methyl alcohol (B-stoff)
        - ME 163 rocket propelled aircraft (burned with H2O2)
- UDMH ((CH3)2 N N H2):
    - Unsymmetrical dimethlyhydrazine
    - Methyl group replaces hydrogen atom
    - Lower freezing point
    - Performance is slightly lower than the performance of hydrazine
    - More stable than MMH
- MMH ((CH3) H N N H2)
    - Monomethylhydrazine

Propellants – Fuels

- Organic Nitrates
  - (ONO2) group + organic radical
  - Very flammable and highly explosive
  - Methyl Nitrate (Monopropellant): liquid
  - Nitrocellulose
    - Solid material of variable composition
    - Empirical formula $C_6H_7O_2(ONO_2)_3$
    - Used in double based solid propellants
    - Low Isp, good explosive (containing its own oxygen)
  - Nitroglycerin ($C_3H_5(ONO_2)_3$):
    - Liquid at room temperature
    - Low Isp
    - Used in the production of dynamite
- Nitroparaffins: NO2 radical replaces one of the hydrogen of the paraffin
  - Nitromathane (CH_3NO_2)
    - Liquid under ambient conditions
    - Monopropellant with fairly good performance (High O concentration in the molecule)
    - Specific density: 1.15
    - Highly toxic
  - Tetranitromethane ($C(NO_2)_4$):
    - Poor performance as a monopropellant (Too much oxygen by mass)

Propellants – Fuels

- Metals:
  - High heat of combustion but limited Isp improvement due to
    - High dissociation, Tc is limited due to dissociation
    - Also high MW of products
- Aluminum (Al):
  - Extensively used as the prime fuel in solid rockets, additive in hybrid rockets
  - Not toxic (can be harmful if inhaled in the dust form)
  - Fairly easy to handle, available and relatively inexpensive in micron size
  - Generally in the powder form
    - Micron size
    - Nano size (low Isp, high efficiency, high burn rate)
  - Enhances the heat of combustion as an additive
    - Effective in energy deficient systems (storable or solid oxidizers)
      - H_2O_2, N_2O, N_2O_4, IRFNA, AP, AN
      - Lower temperature and less dissociation
    - No gain with LOX, energy gain diminishes due to dissociation
- Beryllium (Be):
  - Extremely high energy
  - Powder in crystalline phase
  - Highly toxic, both acute and also chronic, carcinogenic

Propellants – Fuels

- Lithium (Li):
  - Alkali metal, Lightest known metal
  - Brittle crystalline form
  - Reacts vigorously with water
- Magnesium (Mg):
  - Can be obtained in powder form
  - Used in igniter systems when large amount of heat is needed in short time
- Metal Hydrides:
  - Combines the light weight hydrogen with the high energy metals
  - Generally expensive
  - Reactive with water (or moist air)
  - Lithium hydride (LiH):
    - White crystalline
  - Aluminum Hydride (AlH3): Alane - Experimental
  - Lithium Aluminum Hydride (LAH): LiAlH4
  - LHA (Li3AlH6): Experimental
    - Claimed to have high positive heat of formation
    - This claim has not been substantiated

Propellants – Fuels

- Hydrogen (H_2):
  - Use in applications requiring very high Isp performance
  - Requires deep cryogenic operation (Boiling point: 20.5 K)
  - Very low density: specific density of 0.07 close to the boiling temperature
  - Wide exposition range (in terms of O/F)
  - Very high Isp with all oxidizers
  - Ortho to para transformation (exothermic process) at low temperatures increases losses
- Boron (B):
  - High energy release with most oxidizers
  - In the pure form it is either a soft powder (amorphous phase) or hard lustrous crystals (in the crystallizing phase)
  - Boron compounds can be toxic
  - Boron has several valancies
  - Used in the pure form (solid) or in the Boron compounds
  - Boranes:
    - B_2H_6, B_4H_{10}: in gas phase under ambient conditions
    - B_6H_{11}, B_5H_9, B_6H_{10}: in liquid phase under ambient conditions
    - $B_{10}H_{14}$: in solid phase under ambient conditions
    - Boranes are highly toxic

Propellants – Fuels

  - Metal Borohydrides: (Reactive with air)
    - Aluminum Borohydride ($Al(BH_4)_3$)
    - Beryllium Borohydride ($Be(BH_4)_2$)
    - Lithium Borohydride ($Li(BH_4)$)
- Metal Organic Compounds:
  - Compounds containing Metal-Carbon bonds
  - Triethylaluminum (TEA) ($Al(C_2H_5)_3$):
    - Colorless liquid
    - Hypergolic with oxygen (pyrophoric)
    - Commonly used liquid and hybrid systems to heat the cold oxygen
    - Spontaneous combustion when it is exposed to air
    - Intermediate Isp
  - Triethylboron (TEB) ($B(C_2H_5)_3$):
    - Similar to TEA
  - Dimethylberyllium ($Be(CH_3)_2$):
    - Solid crystalline in snow white needles
    - Spontaneously flammable in moist air

Propellants – Fuels

- Hydrocarbons (C_nH_m)
  - Important source of fuels
  - Wide range selection
- Petroleum Fractions
  - Primarily liquids under ambient conditions
  - Kerosene, Jet Fuels JP-1, …JP-10, RP-1
  - Mixtures of hydrocarbons, primarily straight chain alkanes (normal paraffins)
    - Example: Kerosene is approximately $C_{10}H_{22}$
  - Good Isp performance
  - Decent density in the range of 0.75-0.85
  - Readily Available
  - Low cost
  - Easy to handle
  - Low toxicity
  - Paraffin waxes are also petroleum products in the solid phase (primarily mixtures of fully saturated hydrocarbons, normal paraffins)
- Polymers:
  - Long chain molecules formed by addition of a repeat unit (monomer)
  - Thermoplastics, thermosetting, elastomers
  - Elastomers are used as solid rocket binders (HTPB, CTPB, PBAN etc.)
  - Thermoplastics or elastomers are used as hybrid rocket fuels (HTPB, HDPE, PMMA)

Propellants – Fuels

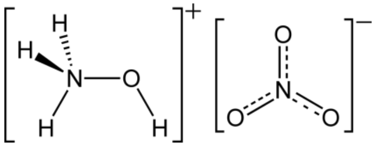
- Fully Saturated Hydrocarbons:
  - No carbon double bonds, molecule has the maximum possible number of hydrogen atoms
  - Series n-alkanes ranging from Methane (CH4) to HDPE polymer
  - Best Isp among the hydrocarbons due to the highest possible hydrogen to carbon ratio
- Unsaturated Hydrocarbons
  - Double or triple carbon bonds branching etc.
  - Reduced Isp due to reduced H/C ratio
- Aromatic Hydrocarbons:
  - Hydrocarbons with a ring structure
    - Benzene (C6H6), naphthalene
    - Poor H/C ratio, poor Isp
- Organic Compounds Containing Oxygen ($C_nH_mO_k$):
  - Alcohols ($C_nH_{2n+1}OH$)
  - Methyl Alcohol (CH3OH)
    - Low performance compared to ethyl alcohol
  - Ethyl Alcohol (C2H5OH)
    - Common liquid rocket fuel
    - Used in the V2 rocket as 75% ethanol + 25% water
    - Specific density is 0.79 at 16 C
    - Intermediate Isp performance
- Ethers (R-O-R): Ethylene Oxide (CH2CH2O): gas under ambient conditions

Properties of Some Liquid Fuels

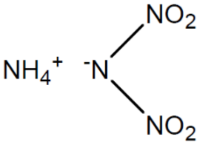
Fuel	Formula	Isp Capability	Density, g/cm3 (Temp K)	Boiling Temp, K	Melting Point, K	Corrosion	Toxicity	Shock Sensitivity
Kerosene	$C_{10}H_{22}$	High	0.8 (298)	-	230	None	Mild	Insensitive
Hydrogen	H_2	Very High	0.071 (20.5)	20.39	13.96	-	None	Insensitive
Ethyl Alcohol	C_2H_5OH	Moderate	0.785 (298)	351.7	158.6	None	Mild	Insensitive
Hydrazine	N_2H_4	High	1.011(288)	386.7	274.7	Slightly	Toxic	Insensitive

Some Promising New Propellants

- Hydroxylamine Nitrate (HAN): $NH_3OH\text{-}NO_3$
  - Ionic salt
  - Oxidizing component
  - Primary use in monopropellant systems



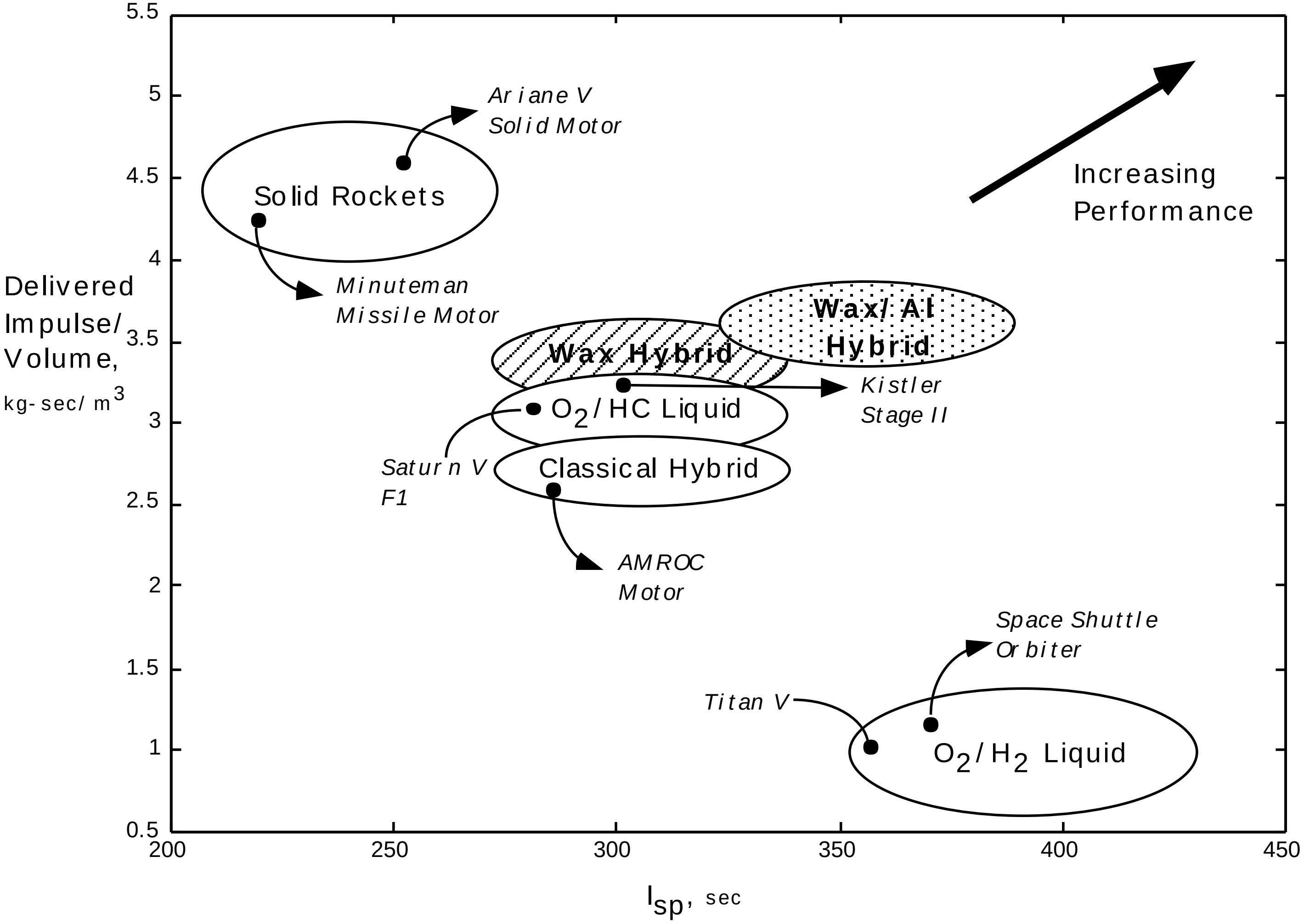
- Ammonium Dinitramide (ADN): $NH_4N\text{-}(NO_2)_2$
  - Inorganic salt
  - Solid rocket oxidizer. Replacement for AP
  - Monopropellant component



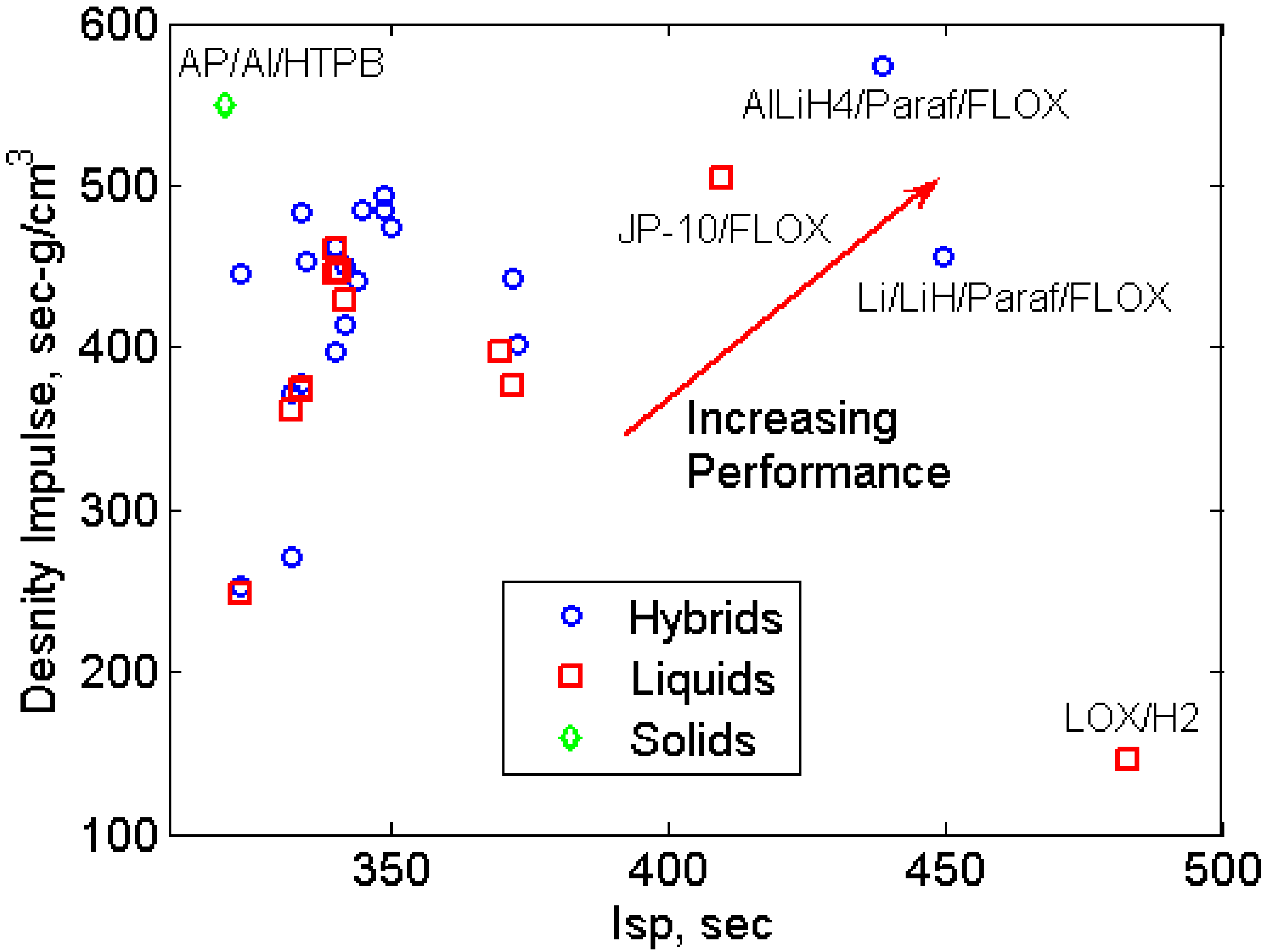
$NH_4^+ \; {}^-N(NO_2)_2$

- Alane: AlH_3
  - Metal hydride
  - Fuel additive for hybrid and solid rockets
  - A phase stabilized version of AlH_3
  - Developed by Russians
  - Not readily available
- Alice: Water Ice/Al mixture
  - Solid rocket propellant

Performance of Chemical Propulsion Systems



Performance of Chemical Propulsion Systems



Propellants – Heating Value for Hydrocarbons

- Consider the stoichiometric reaction of a generic hydrocarbon with oxygen

$$C_nH_m + (n + m/4)\ O_2 \rightarrow n\ CO_2 + \frac{m}{2} H_2O$$

- The heat of reaction (in kcal/mole) can be written as (water in gas phase)

$$\Delta\hat{H}_{R,25C} = \frac{m}{2}\Delta\hat{H}_{fH2O,25C} + n\ \Delta\hat{H}_{fCO2,25C} - \Delta\hat{H}_{fCnHm,25C} = \frac{m}{2}(-57.79) + n\ (-94.05) - \Delta\hat{H}_{fCnHm,25C}$$

- Heating value of fuel is defined as

$$Q_{Fuel} \equiv \frac{\left|\Delta\hat{H}_{R,25C}\right|}{MW_{fuel}}$$

- In the case of generic hydrocarbon reaction with oxygen (water in gas phase)

$$Q_{Fuel} \equiv 1000 \cdot \frac{\left|\frac{m}{2}(-57.79) + n\ (-94.05) - \Delta\hat{H}_{fCnHm,25C}\right|}{12\ n + m} \quad (kcal/kg)$$

- The molecular weight of the products are (with no dissociation)

$$MW_p = \frac{nMW_{CO2} + (m/2)\,MW_{H2O}}{n + m/2} = \frac{44n + 9m}{n + m/2} \quad (g/mole)$$

- m/n ratio must be high to maximize the heating value and to minimize the molecular weight of the products

Propellants – Heating Value for Hydrocarbons

- For normal alkanes (Fully saturated hydrocarbons)

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 \rightarrow n\ CO_2 + (n+1)H_2O$$

- Heating value becomes

$$Q_{Fuel} \equiv 1000 \cdot \frac{\left|(n+1)(-57.79) + n\ (-94.05) + 17.89 + 5.00\ (n-1)\right|}{14n+2} = 1000 \cdot \frac{\left|-146.84n - 44.9\right|}{14n+2} \quad (kcal/kg)$$

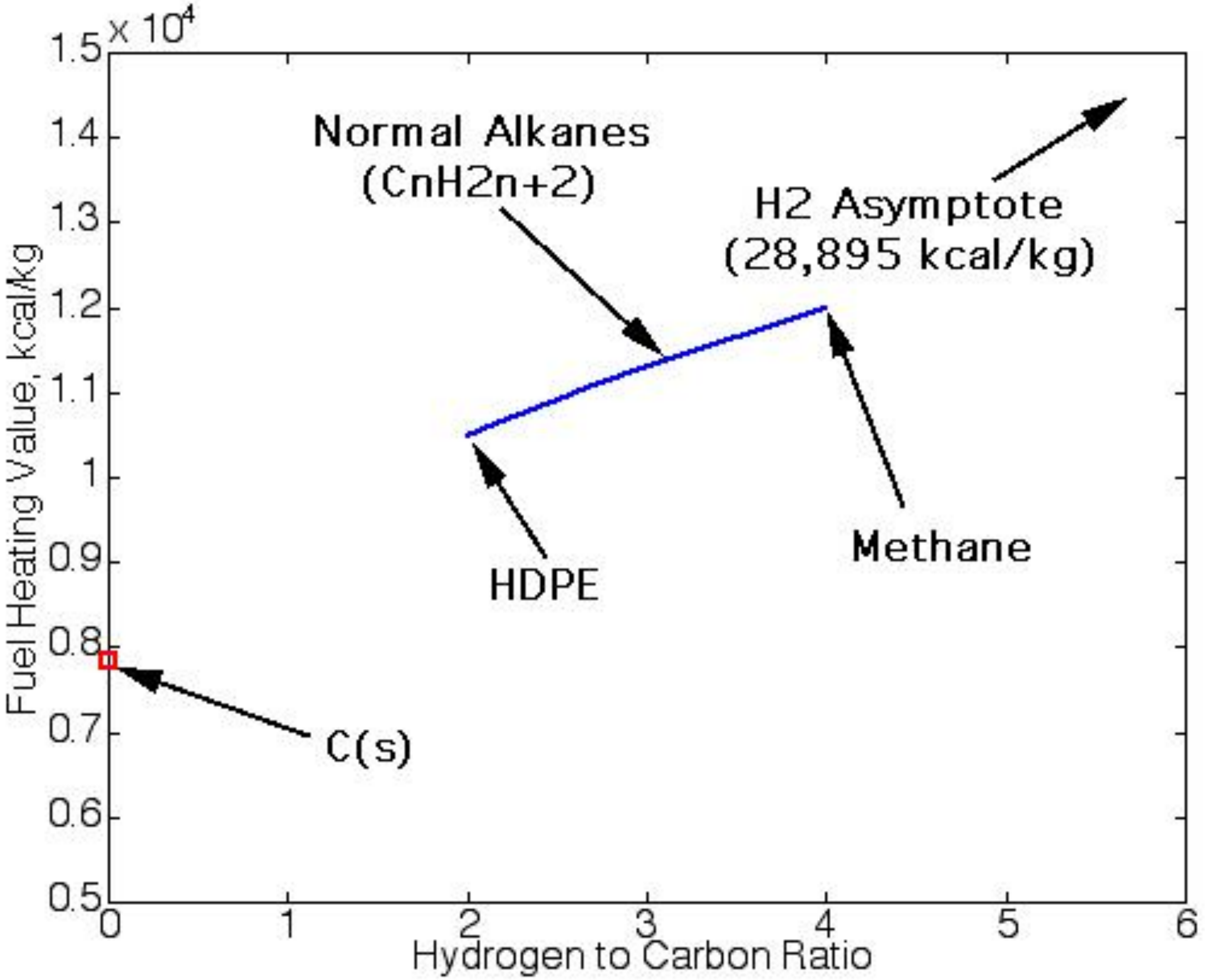
- The molecular weight of the products are (with no dissociation)

$$MW_p = \frac{62n+18}{2n+1} \quad (g/mole)$$

- Fully saturated hydrocarbons have the best possible m/n ratio for given carbon numbers in the hydrocarbon molecule
- The asymptotic values are (HDPE polymer)

$$\lim_{n\to\infty} MW_p \rightarrow 31.0 \quad (g/mole) \qquad \lim_{n\to\infty} Q_{Fuel} \rightarrow 10{,}490 \ \ (kcal/kg)$$

Heating Value of Fuels vs Hydrogen to Carbon Ratio



Propellants – Heating Value for Hydrocarbons with Other Oxidizers

- Consider the stoichiometric reaction of a generic hydrocarbon with N2O

$$C_nH_m + (2n+m/2)\ N_2O \rightarrow n\ CO_2 + \frac{m}{2}H_2O\ + (2n+m/2)\ N_2$$

- The heat of reaction (in kcal/mole) can be written as

$$\Delta\hat{H}_{R,25C} = \frac{m}{2}(-57.79) + n\ (-94.05) - \Delta\hat{H}_{fCnHm,25C} - (2n+m/2)\ (19.61)$$

- Compared to oxygen, the heat of reaction is higher (on molar base) but the adiabatic flame temperature is lower due to the dilution effect of the molecular nitrogen
- Also N2 increases the average MW of the products
- Thus c* and Isp are lower with N2O
- Consider the stoichiometric reaction of a generic hydrocarbon with diluted oxygen

$$C_nH_m + \left(2n+\frac{m}{2}\right)\left(\frac{1}{2}O_2 + N_2\right) \rightarrow n\ CO_2 + \frac{m}{2}H_2O\ + \left(2n+\frac{m}{2}\right)\ N_2$$

- The heat of reaction in kcal/mole

$$\Delta\hat{H}_{R,25C} = \frac{m}{2}(-57.79) + n\ (-94.05) - \Delta\hat{H}_{fCnHm,25C} - (2n+m/2)\ (0)$$

- No help from the oxidizer molecules
- Thus the c* and Isp are expected to be lower

Propellants – Effect of Oxidizer in the Fuel Molecule

- Consider the stoichiometric reaction of methane with N2O

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

- The heating value is

$$Q_{Fuel} = 1000 \cdot \frac{\left|2(-57.79) + (-94.05) + 17.89\right|}{16} = 11{,}980 \ \ (kcal/kg)$$

- Define a propellant based heating value (Same as available energy)

$$Q_{prop} = \frac{\left|\Delta \hat{H}_{R,25C}\right|}{MW_{fuel} + 2\,MW_{ox}} = 2{,}396 \ \ (kcal/kg)$$

- Consider methanol combustion

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

- Note that stoichiometric O/F ratio is reduced to 1.5 from 4 for methane
- Fuel and propellant heating values are

$$Q_{Fuel} = 1000 \cdot \frac{\left|2(-57.79) + (-94.05) + 57.02\right|}{16} = 4{,}770 \ \ (kcal/kg)$$

$$Q_{prop} = \frac{\left|\Delta \hat{H}_{R,25C}\right|}{MW_{fuel} + 3\,MW_{ox}/2} = 1{,}908 \ \ (kcal/kg)$$

- Note that available energy has been reduced by 20%.

Propellants – Effect of Metal Additives

- Consider the stoichiometric reaction of methane with N2O

$$CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O + 4N_2$$

- Stoichiometric O/F is 11.0. The heating values of the fuel and the propellant are

$$Q_{Fuel} = 1000 \cdot \frac{\left|2(-57.79) + (-94.05) + 17.89 - 4(19.61)\right|}{16} = 16{,}886 \ \ (kcal/kg)$$

$$Q_{prop} = \frac{\Delta\hat{H}_{R,25C}}{MW_{fuel} + 4\,MW_{ox}} = 1{,}407 \ \ (kcal/kg)$$

- Consider the stoichiometric reaction of methane with 40% aluminum by moles

$$\left(CH_4 + 0.4Al\right) + 4.6N_2O \rightarrow CO_2 + 2H_2O + 0.2Al_2O_3 + 4.6N_2$$

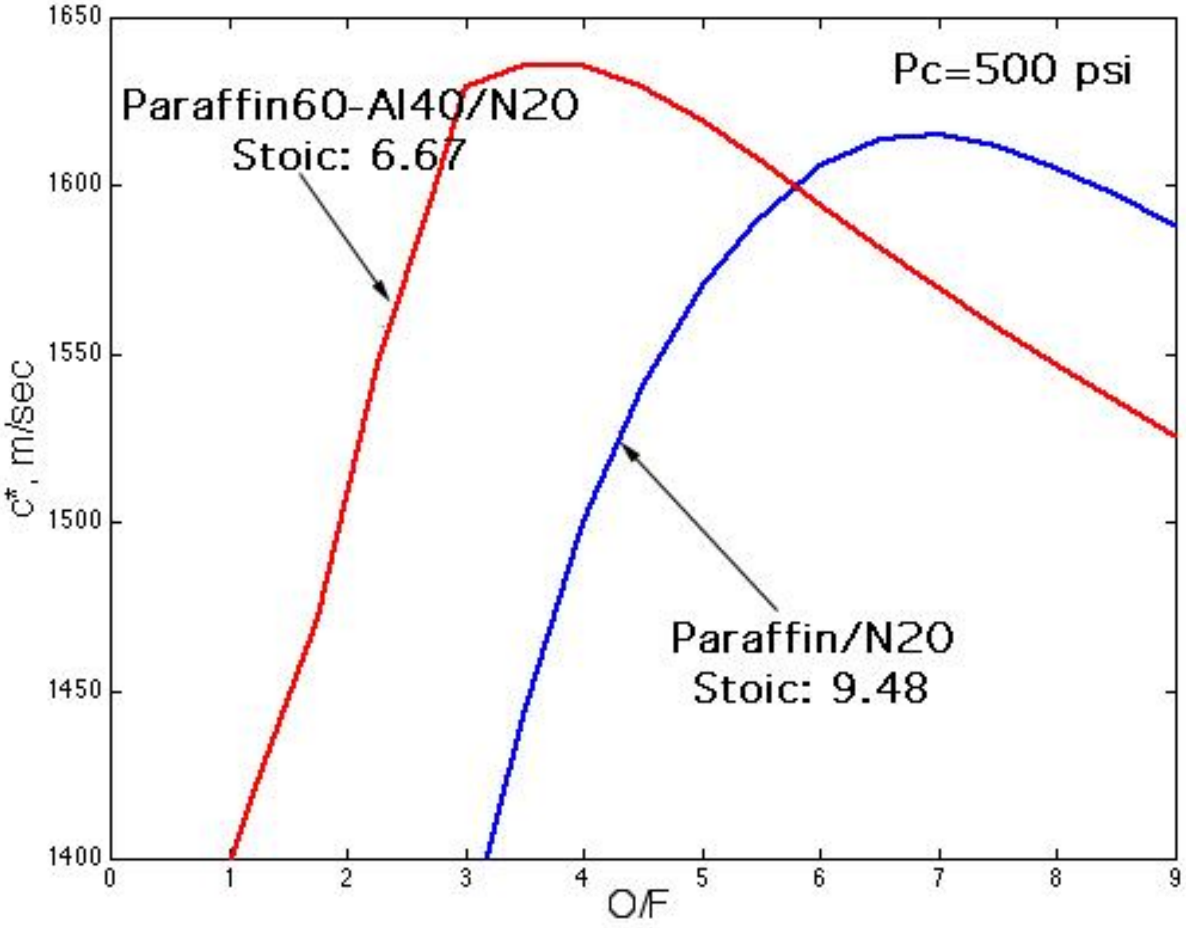
- Stoichiometric O/F is reduced to 7.55 from 11.0. The heating values of the fuel and the propellant are

$$Q_{Fuel} = 1000 \cdot \frac{\left|2(-57.79) + (-94.05) + 0.2(-399.1) + 17.89 - 4.6(19.61)\right|}{26.8} = 13{,}499 \ \ (kcal/kg)$$

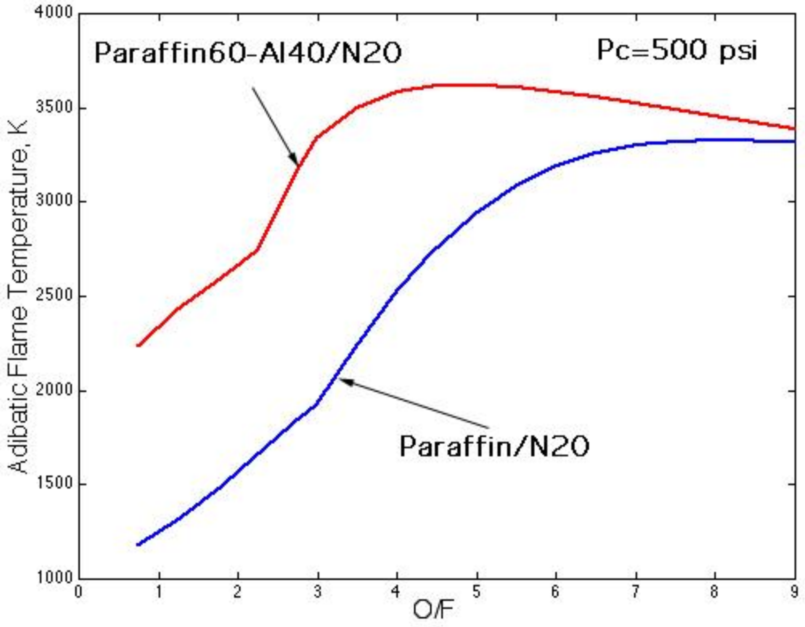
$$Q_{prop} = \frac{\Delta\hat{H}_{R,25C}}{MW_{CH4} + 0.4\,MW_{Al} + 4.6\,MW_{ox}} = 1{,}578 \ \ (kcal/kg)$$

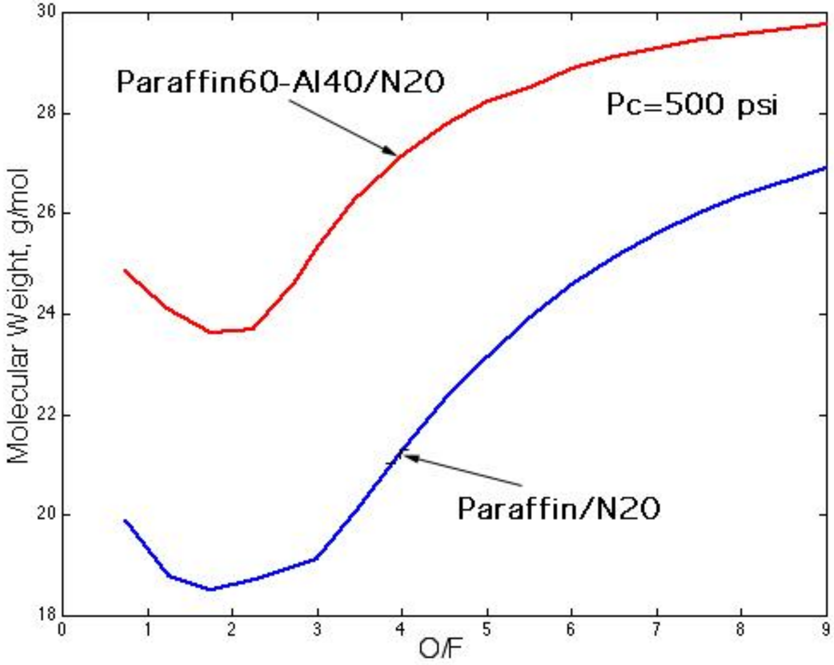
- Note that heating value for the propellant is increased by approximately 13%.

Effect of Al Addition on C* (Paraffin as the baseline material)

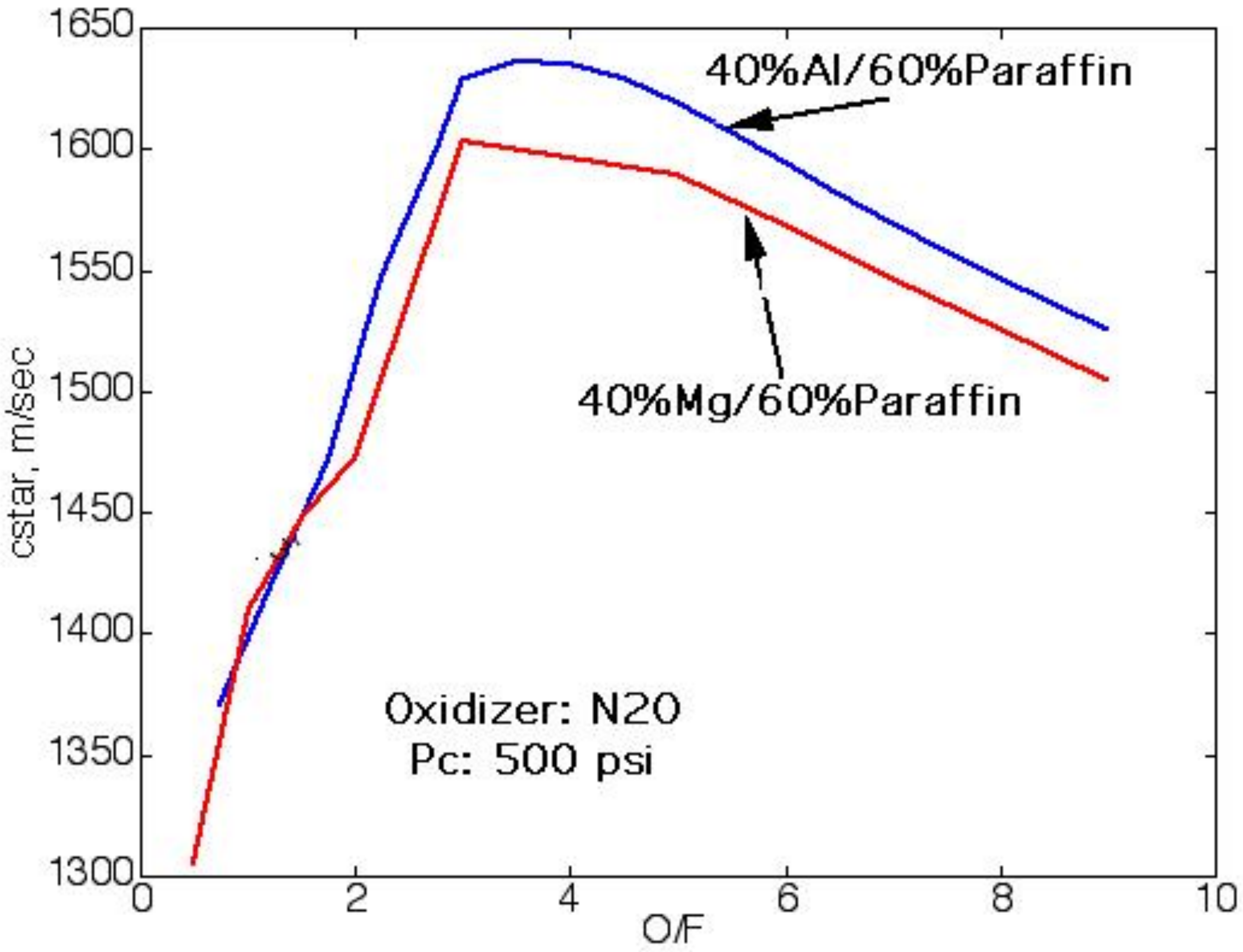


Effect of Al Addition on Tc and MW

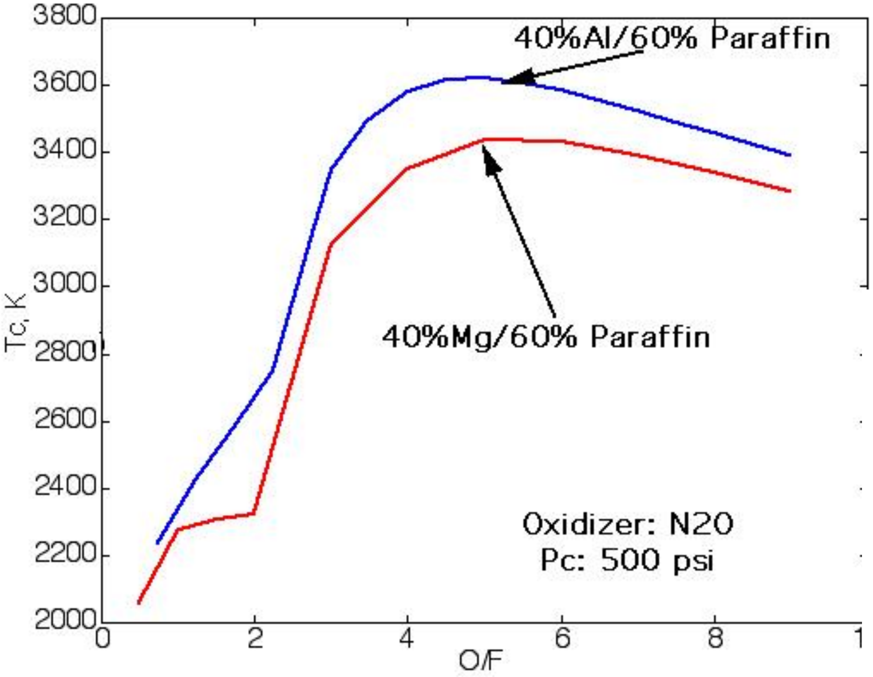


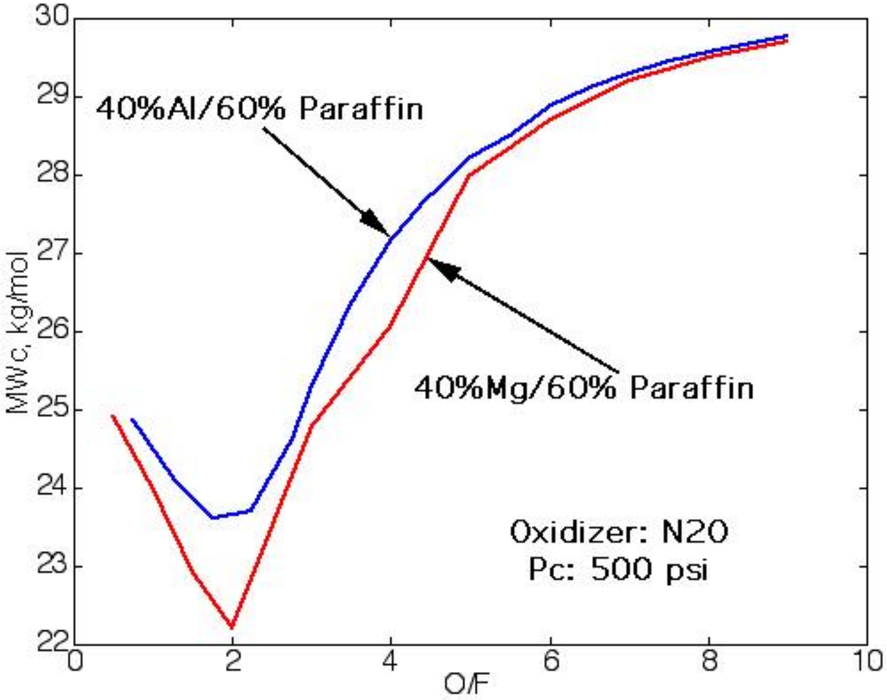


Performance Comparison Al vs Mg-Oxidizer N2O



Performance Comparison Al vs Mg-Oxidizer N2O





Propellants – Conclusive Remarks

- Oxidizers:
  - Common oxidizers that are currently being used:
    - Cryogenic: LOX
    - Storable: N2O4, N2O, IRFNA
    - Solid: AP, AN
  - Experimental oxidizers:
    - Gellified oxidizers, (GIRFNA)
    - H2O2 at various concentrations
    - HAN, ADN
  - LOX is a high energy oxidizer but it is cryogenic
  - Storable and solid oxidizers have lower performance compared to LOX
- Fuels:
  - Common fuels are
    - Kerosene, RP-1, Ethanol, N2H4 (Liquids)
    - Polymers, Al (Solids)
    - Polymers (Hybrids)
    - All hydrocarbons including the polymers have similar performance
    - N2H4 have better performance but highly toxic
- Propellant selection requires a balance between the practical issues (toxicity, cost) and performance
- Isp Performance
  - Be careful when comparing the Isp performance of propellants since Isp strongly depends on the area ratio, chamber pressure, ambient pressure, nature of the equilibrium assumption
  - c* is probably a better method of comparing propellants. Only weak chamber pressure dependence

N2O Safety Issues

Nitrous Oxide – Introduction

Physical

A saturated liquid at room temperature. Self pressurizing liquid (744 psi @ 20 C)

Two phase flow in the feed system (complicated injector design)

Highly effective green house gas (Global Warming Potential: 300 x CO_2)

Chemical

Oxidizing agent.

Monopropellant. Positive heat of formation. Decomposes into N_2 and O_2 by releasing significant amount of heat

$$N_2O \rightarrow N_2 + 1/2\, O_2 + 19.61\ kcal/mole$$

Highly effective solvent for hydrocarbons

Biological

Mildly toxic. Anesthetic and analgesic agent still used in medicine, “Laughing gas”

Nitrous Oxide Uses

- Oxidizer: Rocket propulsion, motor racing
- Anesthetic Agent: Medicine, dentistry
- Solvent
- Aerosol propellant: Culinary use (in whip cream dispensers)
- Etchant :Semiconductor industry

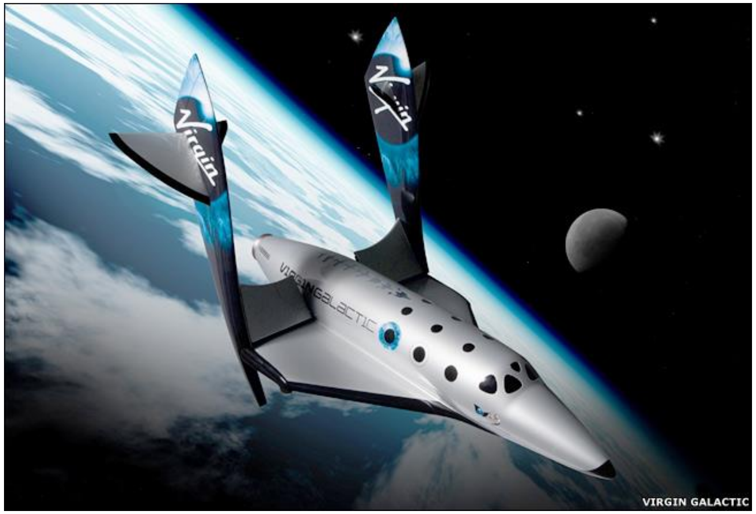
Nitrous Oxide – SpaceShipTwo

Sub-orbital Space Tourism

Virgin Galactic has contracted Scaled Composites to build SpaceShipTwo

SpaceShipTwo design uses a N_2O based hybrid rocket

Testing of the propulsion system started in summer 2007



Explosion at Scaled Composites facility in Mojave Airport on July 26, 2007 during a cold flow test with N_2O

Nitrous Oxide – Explosion Hazard

SPG Experience

Small N_2O/paraffin motor

First N_2O explosion in February 2006

Many small explosions in the feed system – minor damage to hardware

Industrial Accidents

N_2O used as solvent for hydrocarbons

Welding full N_2O tanks

Heating source tanks with open flames

Medical Accidents

Many medical explosions reported in operating theater
  - Found 10 cases (3 fatal)

Intestinal/colonic explosions during diathermy
  - High content of H_2 and CH_4 in the intestines and colon
  - The concentration of N_2O increases significantly in the body cavities following its application as an anesthetic

Car Exploded in Garage

LATEBREAKERSLATEBREAKERSLATEBREAKERS

the big bang theory

AT some point in our short life we've all been notified of the impending end of the world. For US residents Doyle and Victoria Schoenberger, it happened for them at exactly 4.30 pm, on Saturday, September 4, 1999.

The Schoenbergers were rocked by an explosion in the garage of their house. The nitrous bottle in their 91 Nissan had exploded after the safety pressure release valve failed following the bottle heater being accidentally left on.

The noise was heard for miles and would certainly have left a ringing in people's ears, especially the Schoenbergers. Just imagine their shock when they went downstairs to see what all the racket was. The first thing that hinted all was not well was seeing the Nissan's boot lid punched through their garage door. Further inspection revealed the true horror. The whole rear of the car was blasted open and looked very much like a peeled banana.

Check out www.enhancedhealth.com/nitrous-express.htm. You won't believe your eyes.

THERE wasn't much left of Doyle Schoenberger's Nissan when his nitrous bottle exploded while it was parked in the garage. It made a hell of a mess of the car, as well as the garage, and there wasn't much left of the bottle.

Problem Statement Objectives and Approach

Problem Statement

N_2O is a promising oxidizer for small, cost effective propulsion systems with moderate performance requirements

Lack of understanding of the decomposition process for N_2O hinders the development of large scale propulsion systems

Hard to quantify the hazard

Objectives

Evaluate the decomposition hazard for N_2O with emphasis on propulsion systems

- Large scale storage at room temperature in non DOT tanks
- Intense flow fields
- Abundance of ignition sources

Compare the hazard to other common monopropellants

Establish a set of recommendations for safe use of N_2O

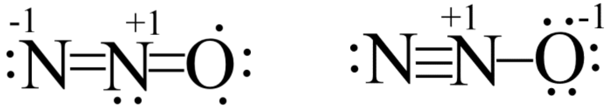
Approach

Kinetics model for the decomposition process

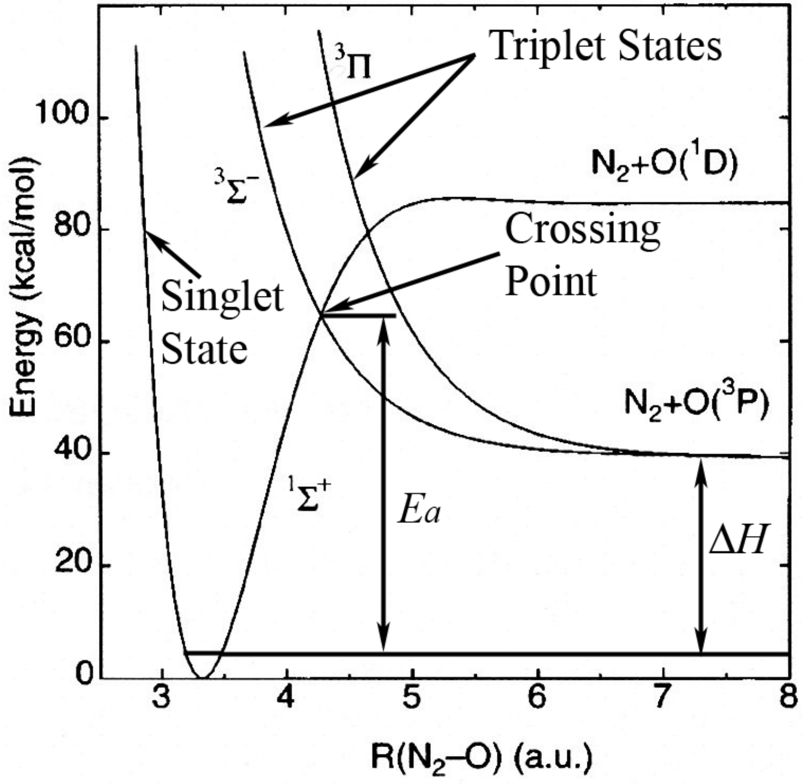
Ignition: Homogenous and local forced

Decomposition in closed vessels

N_2O Decomposition Physics



Resonant structure



Ref.:*Stearn and Eyring (1935)*

N_2O decomposition follows the elementary unimolecular reaction

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

This reaction is considered “abnormal” since it requires a change in multiplicity from a singlet state to a triplet state.

This change in multiplicity is forbidden by the quantum mechanics

The transmission can only take place through “tunneling” resulting in a reduced transmission rate

The reaction rate for N_2O is 1-2 orders lower than the reaction rate predicted for a “normal” unimolecular reaction (such as the decomposition of H_2O_2)

This quantum mechanical effect plays a role in the relative safety of N_2O

N_2O Decomposition Kinetics

The decomposition of N_2O is believed to follow the elementary reactions:

- Decomposition reaction

$$\mathrm{N_2O + M \xrightarrow{k_1} N_2 + O + M}$$

- Reactions involving atomic oxygen radical

$$\mathrm{N_2O + O \xrightarrow{k_2} NO + NO} \qquad \mathrm{N_2O + O \xrightarrow{k_3} N_2 + O_2}$$

$$\mathrm{O + O + M \xrightarrow{k_4} O_2 + M} \qquad \mathrm{O} + wall \xrightarrow{k_{4w}} 1/2\,\mathrm{O_2} + wall$$

- Following reactions play a secondary role (i.e. self-limiting of NO)

$$\mathrm{NO + O + M \xrightarrow{k_5} NO_2 + M} \qquad \mathrm{N_2O + NO_2 \xrightarrow{k_6} N_2 + O_2 + NO}$$

$$\mathrm{NO_2 + O \xrightarrow{k_7} NO + O_2} \qquad \mathrm{NO + N_2O \xrightarrow{k_8} N_2 + NO_2}$$

Lindemann's Theory

Physical steps of the first reaction are

$$N_2O + M \xrightarrow{k_a} N_2O^* + M$$

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

$$N_2O^* \xrightarrow{k_b} N_2 + O$$

Steady-state assumption for the excited complex [N_2O^*] results in the following kinetic equation

$$-\frac{d[N_2O]}{dt} = m\frac{k_a k_b [N_2O][M]}{k_b + k_{-a}[M]}$$

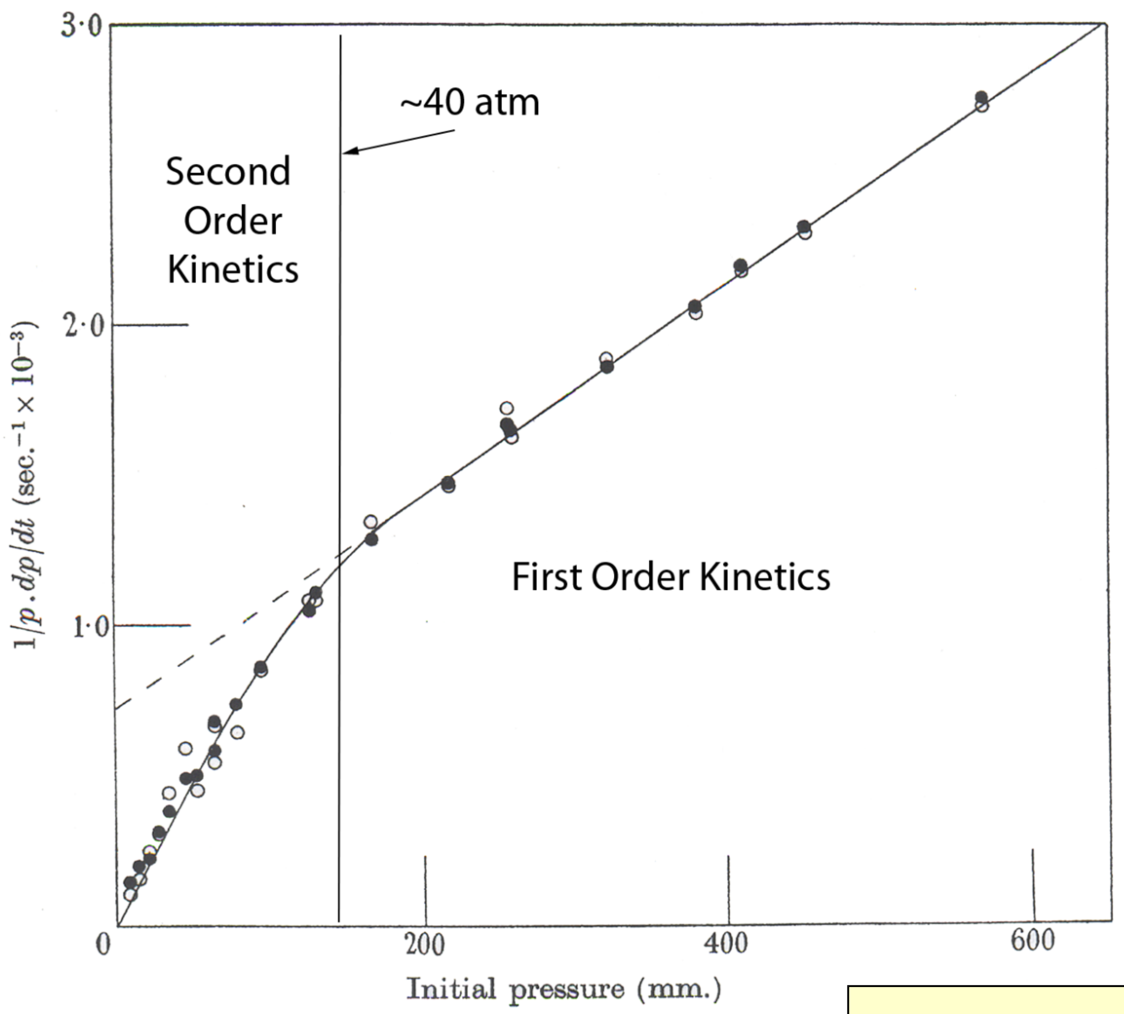
At high pressures the reaction becomes first order

$$-\frac{d[N_2O]}{dt} = m\frac{k_a k_b}{k_{-a}}[N_2O] = m k_1^{\infty}[N_2O]$$

At low pressures the reaction is second order

$$-\frac{d[N_2O]}{dt} = m k_a [N_2O][M] = m k_1^{o}[N_2O][M]$$

Reaction Order Data



Data follows the Lidemann's theory in general

For pressures larger than 40 atm (~600 psi) the reaction is shown to be first order

Note that for the first order reaction the collision partner [M] does **NOT** play a role greatly simplifying the analysis

Ref.:*Lewis and Hinshellwood (1938)*

N_2O Simplified Kinetic Model

A simplified one step first order kinetic model can be developed at high pressures

Steady-state assumption for [O] results in the following kinetic equation for the decomposition of N_2O

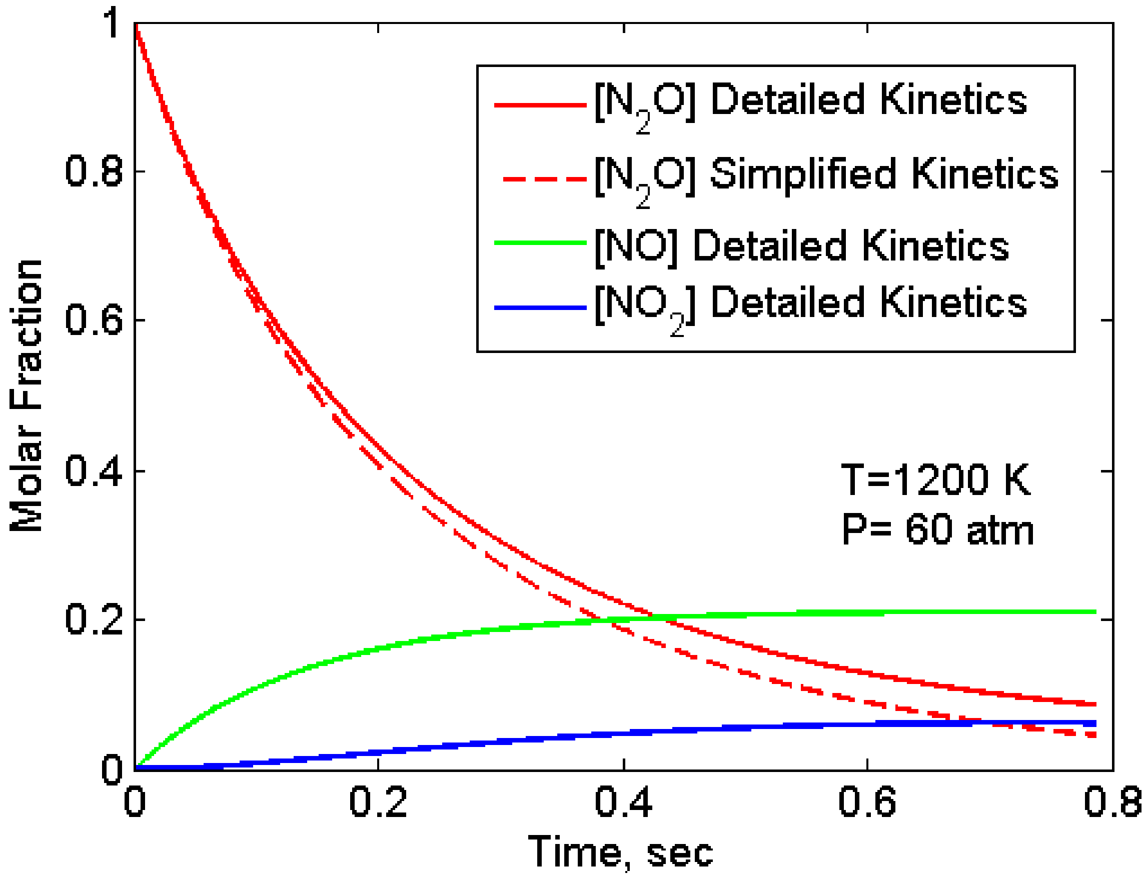
$$-\frac{d[N_2O]}{dt} = m k_1 [N_2O][M]$$

- *m=2* for slow recombination reactions 4 and 4w
- *m=1* for fast recombination reactions 4 and 4w

At high pressures (from Lidemann's theory)

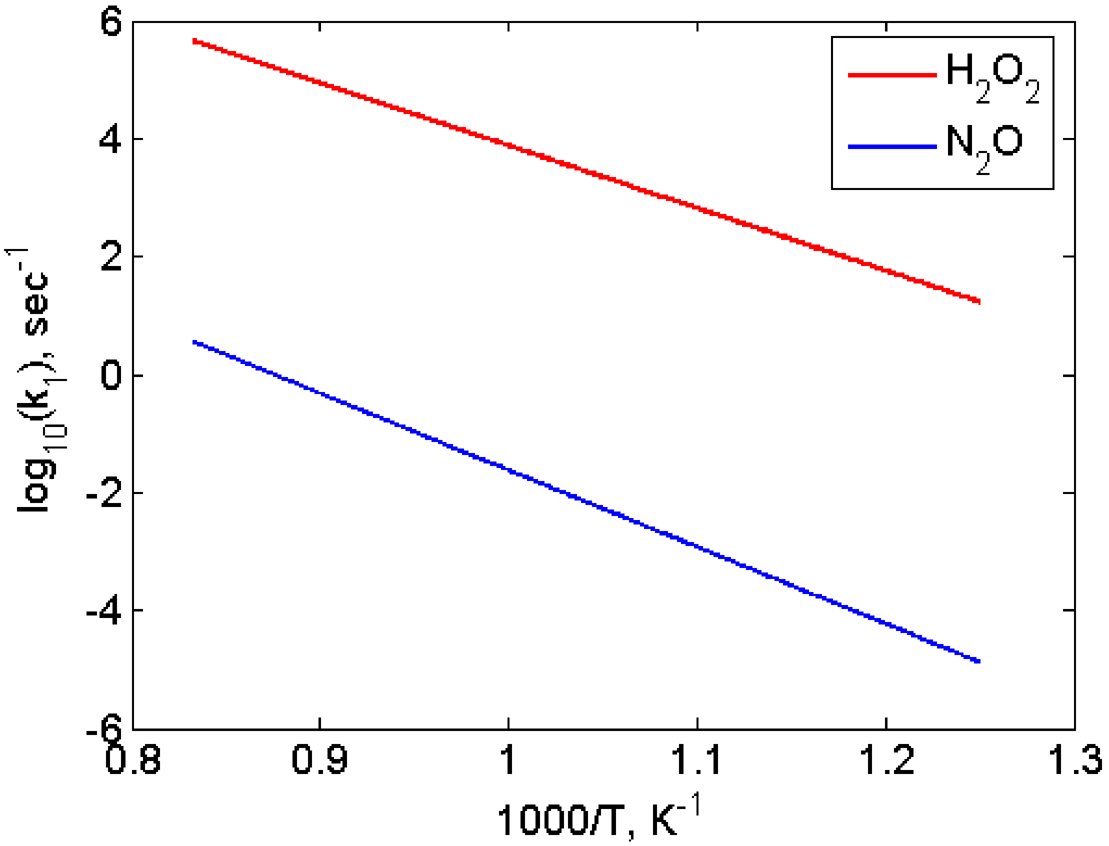
$$-\frac{d[N_2O]}{dt} = m k_1^{\infty} [N_2O] \qquad k_1^{\infty}(T) = 1.3\text{x}10^{11}\, e^{-30{,}000/T} \quad s^{-1}$$

Detailed Kinetics vs Simplified Kinetics



- Simulations using the detailed kinetics set has been conducted
- Simplified first order model agrees well with the detailed kinetics predictions
- Agreement gets better as the wall recombination reaction becomes less dominant
- Significant quantities of NO is formed

Decomposition: N_2O vs H_2O_2



Decomposition characteristics of two energetic oxidizers

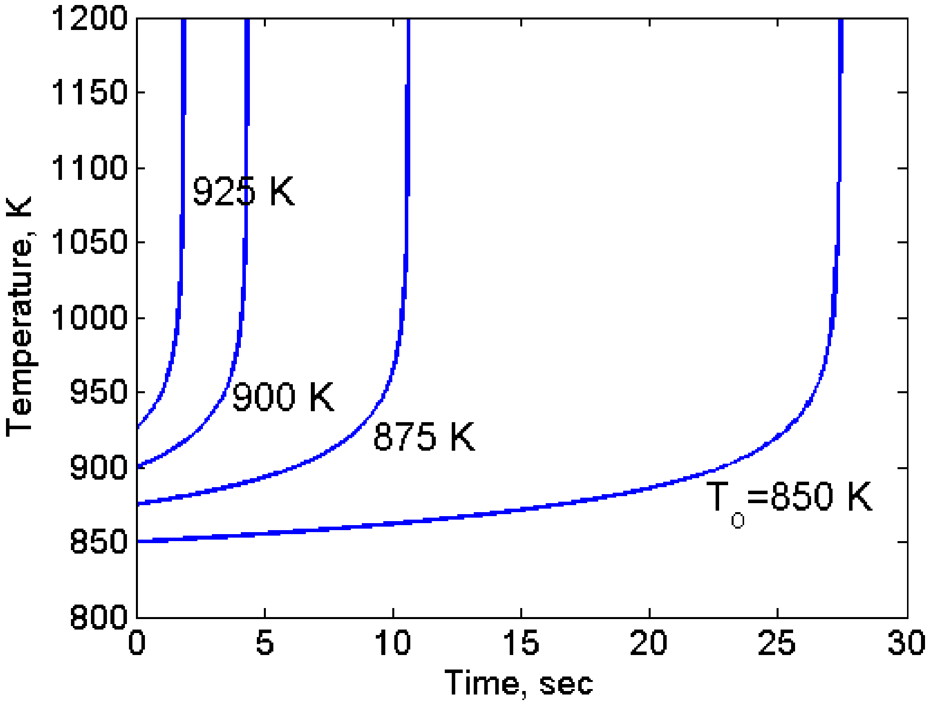
Decomposition of H_2O_2 also follows first order kinetics at high pressures

H_2O_2 decomposition rate is **six orders of magnitude** larger than the rate of N_2O decomposition

- Half of this comes from the "abnormal" nature of N_2O decomposition
- The remainder is due to the larger activation energy

This explains the observed relative safety of N_2O compared to H_2O_2

Homogenous Ignition



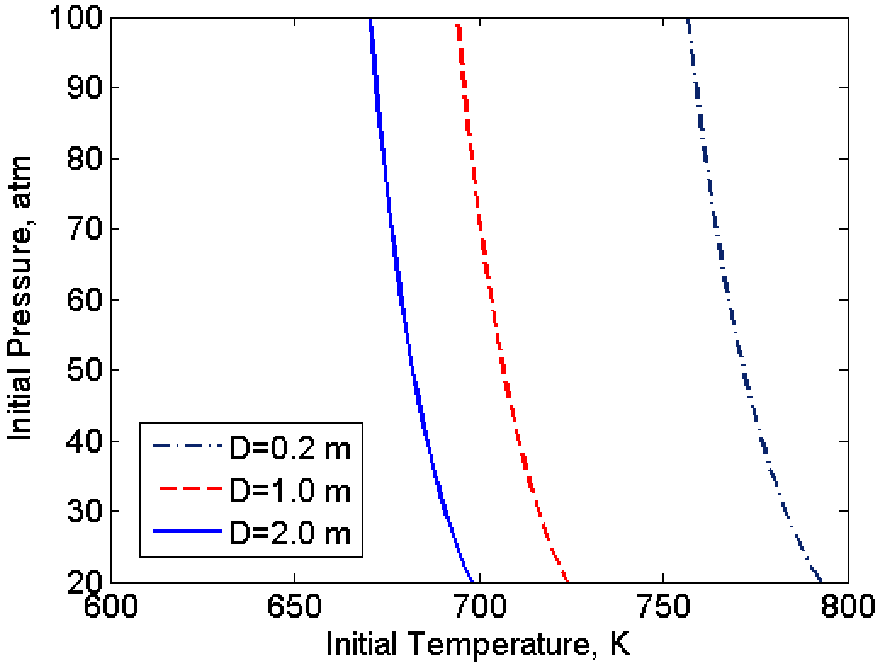
Temperature is uniformly increased in the bulk of N_2O vapor

Heat is generated by reaction and removed by heat transfer

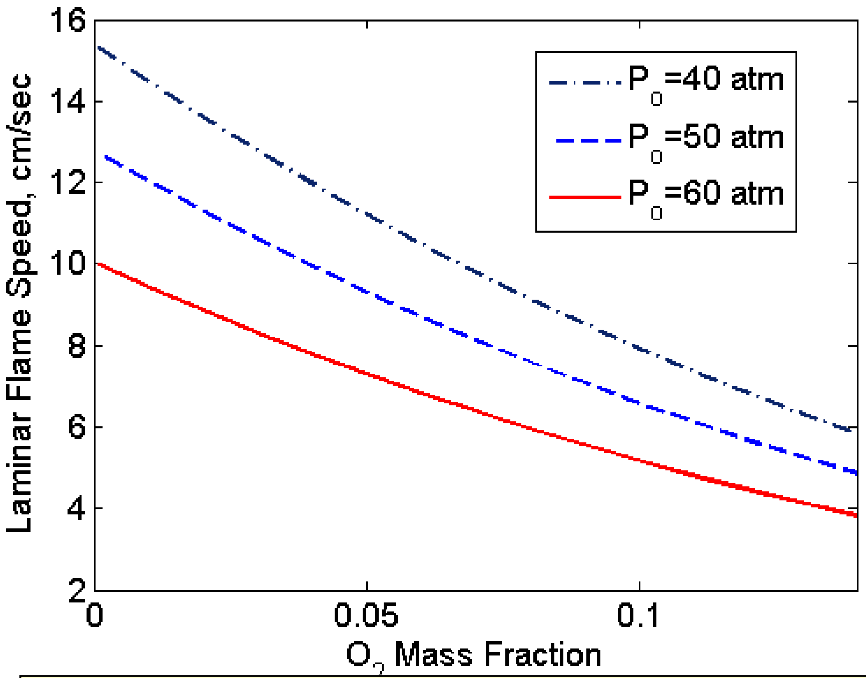
Induction times are too long to be practical for temperatures less than **850 K**

Explosion boundaries can be established in the *P-T* plane for a given vessel size and composition

The ignition temperatures are quite high even for very large vessels



Local Thermal Ignition



N_2O vapor is locally heated to high temperatures resulting in the propagation of a self sustained deflagration wave

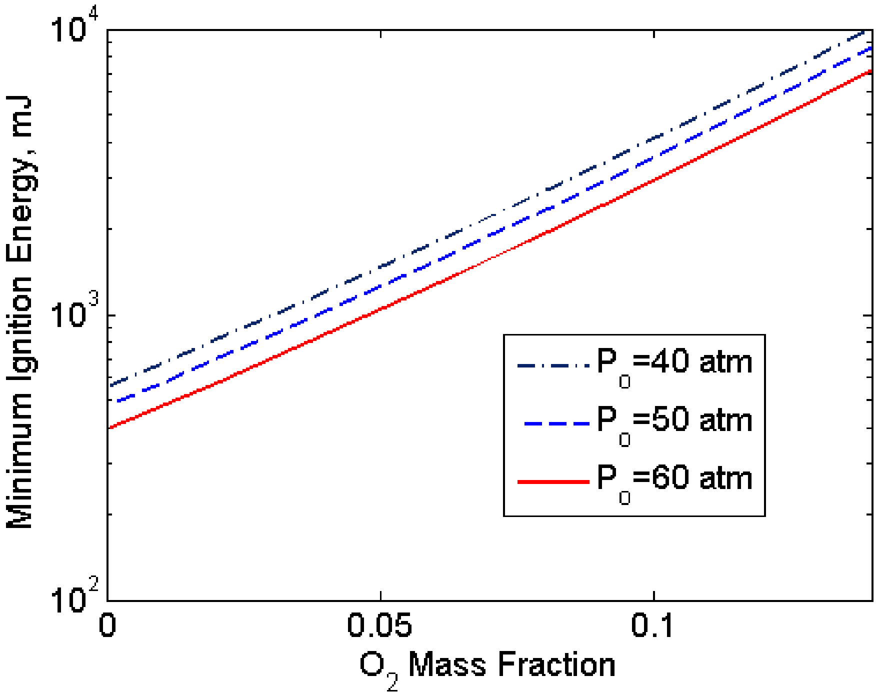
The laminar flame speed in pure N_2O is quite low ~10-15 cm/sec

Reduces with pressure and dilution

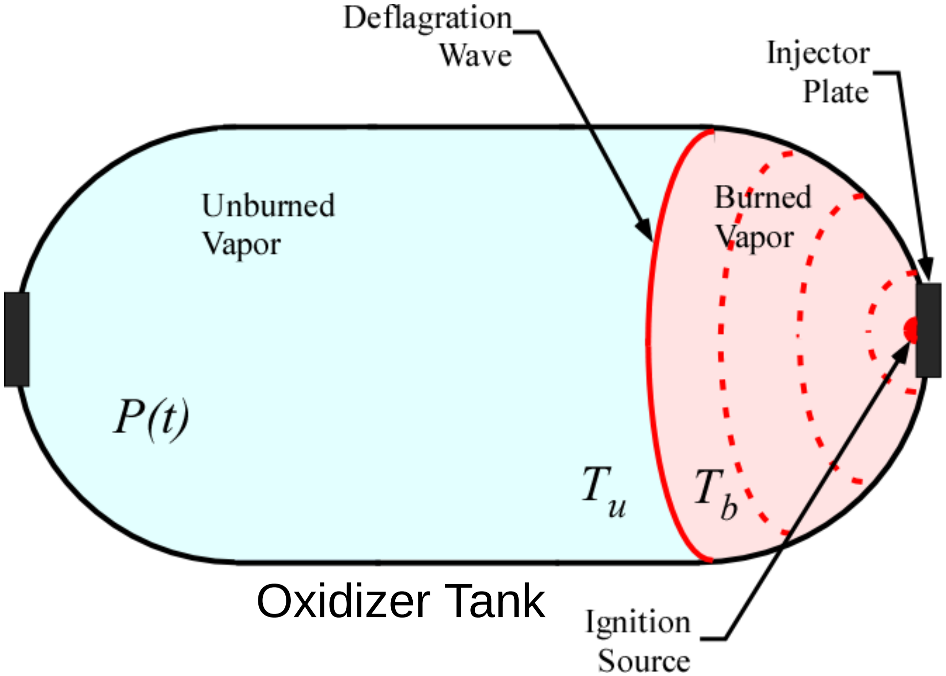
The minimum ignition energy for N_2O is around 450 mJ

This is 3 orders of magnitude larger than the ignition energy for stoichiometric CH_4/air flame

At high dilution levels this mixture is virtually impossible to ignite



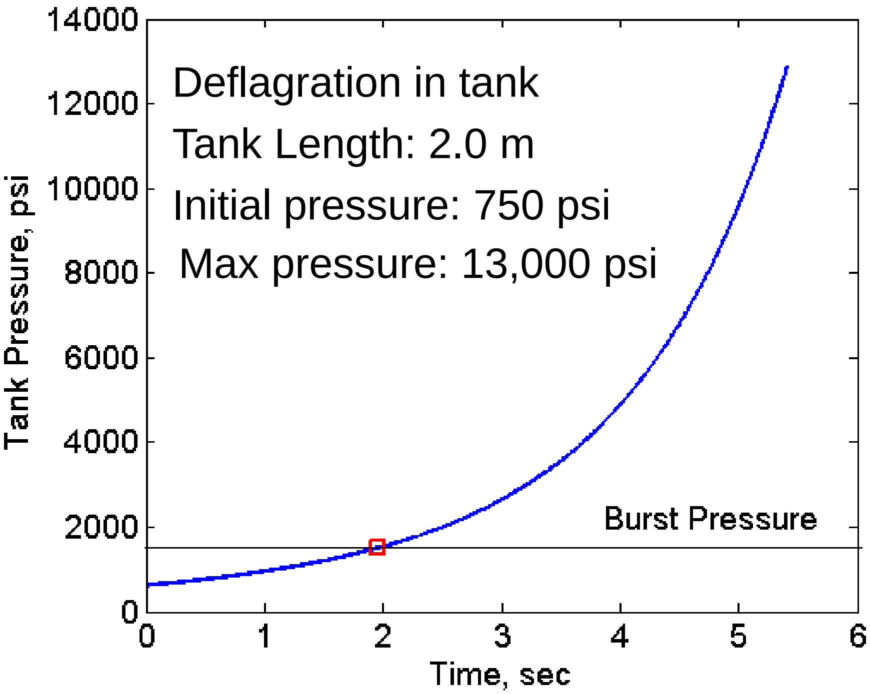
N_2O Decomposition Hazard



Oxidizer Tank

Largest hazard is in the oxidizer tank during vapor phase combustion

An ignition source (hot injector plate) could start a combustion wave which would result in significant pressure increase


Deflagration in tank

Tank Length: 2.0 m

Initial pressure: 750 psi

Max pressure: 13,000 psi

Pressure ratio is quite high, around 20

Burst pressure is a fraction of P_{max}

Time scales is seconds

Risk Mitigation

Supercharge with inert gas (He)

Incorporate a pressure relief system

N_2O Safety Recommendations

Nitrous oxide is an energetic material and it must be respected!

- Follow strict procedures to protect personnel during tests/operations
- Conduct a hazard analysis

Supercharge N_2O run/flight tanks. N_2O in blow down mode is inherently hazardous

Especially for manned systems implement a well tested pressure relief system

For small scale testing keep the run tank in the vertical position

Follow strict oxidizer cleaning procedures

Only use compatible materials. Most hydrocarbons are **NOT** compatible

Ignition should lead the N_2O flow into the combustion chamber

Avoid catalytic materials

Remember the quote: “Ignition Source is Always Free”

Concluding Remarks

All attempts to ignite N_2O in the liquid phase have **failed**

N_2O in the vapor phase can **NOT** support detonation

Even very small levels of fuel contamination changes the dynamics!

Despite its wide use, the number of decomposition related accidents for N_2O is very limited in number

This is due to its abnormally slow kinetics. For example N_2O kinetics is approximately **million times** slower than the rates of H_2O_2

Use of N_2O in propulsion applications presents unique hazards

- Large quantities at room temperature
- Intense flow fields
- Abundance of ignition sources

If handled right, nitrous oxide is one of the safest oxidizers that can be used in propulsion applications