AA 284a
Advanced Rocket Propulsion

Lecture 3
Rocket Propellants

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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)

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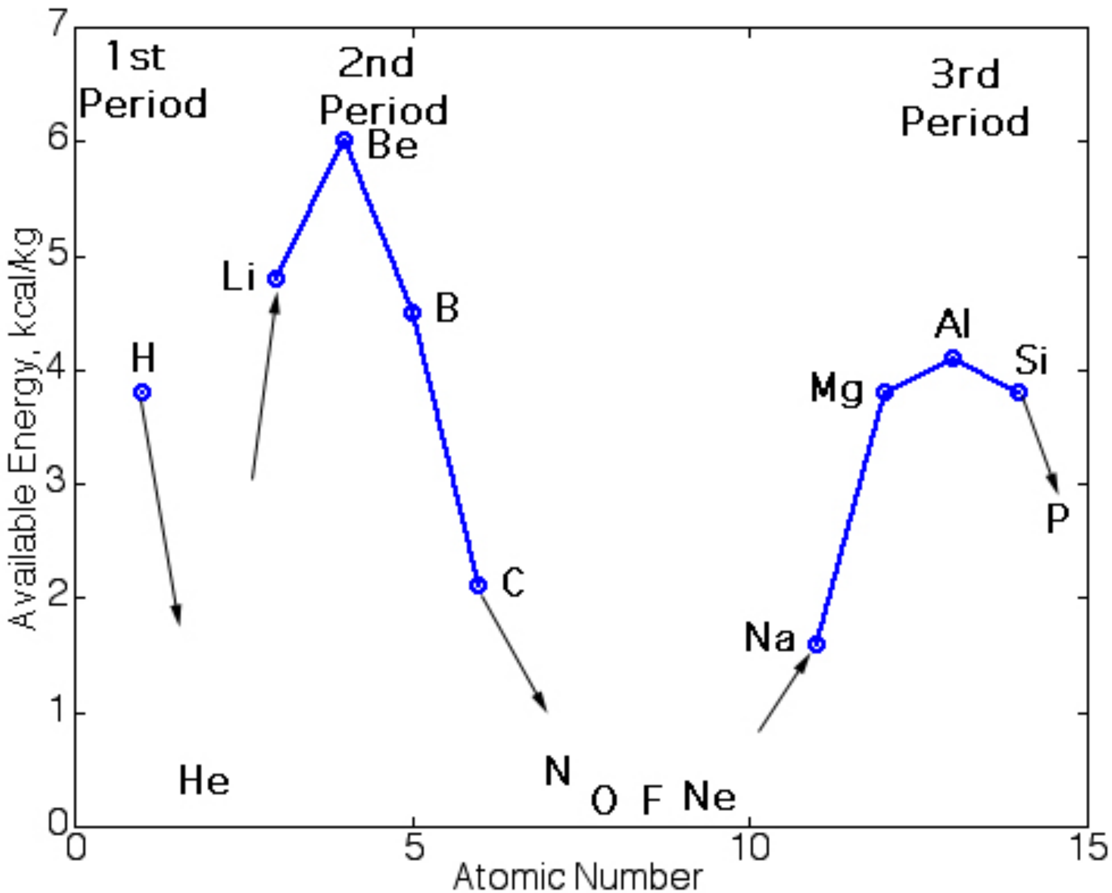
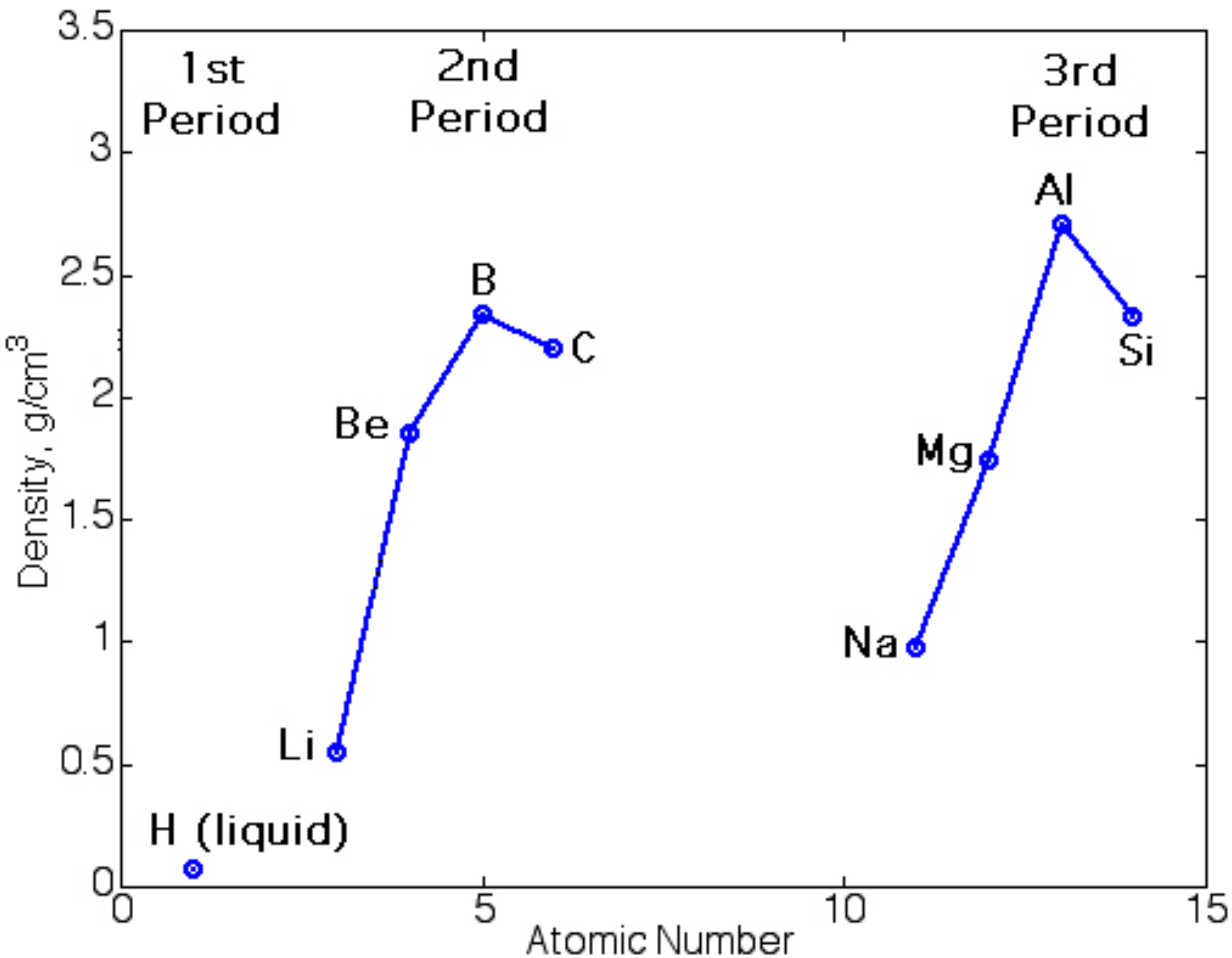
Propellants – Available Heat of Reaction for light elements with O2 at Stoichiometric Mixture



- 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 – 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) – LOX [In Use]

- 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

Space Shuttle Main Engine H2/LOX (Liquid Rocket)

Propellants – Oxidizers

Fluorine (F_2) [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 O_2)
  - With carbon containing fuels, Isp is lowered due to heavy CF_4 formation
  - Mixed with O_2 at various concentrations to minimize the CF_4 formation (FLOX)
- Cryogenic- Low boiling point 85.24 K, yellow colored liquid in condensed phase
- Denser than O_2: 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

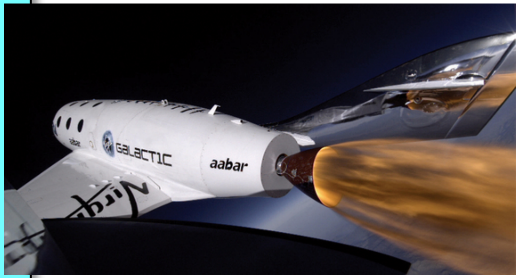
Propellants – Oxidizers

Nitrogen Oxides

Nitrous Oxide (N_2O) [In 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
- Commonly used in the hybrid rocket propulsion systems (systems with low Delta V requirements)
  - SpaceShipOne, SpaceShipTwo, 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)

SpaceShipOne and SpaceShipTwo (Hybrid Rockets)



Propellants – Oxidizers

Nitrogen Oxides:

Nitrogen Tetroxide (N2O4) [In Use]

- 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.

Titan IVB
Core Propulsion

Propellants – Oxidizers

Hydrogen Oxides

Hydrogen Peroxide (H2O2) [In Use]

- 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

Black Knight British LV

Propellants – Oxidizers

Nitric Acid (HNO_3): [In Use]

- Widely used as an oxidizer (Especially internationally)
- Anhydrous Nitric Acid: (> 99.0% HNO_3)
- White Fuming Nitric Acid (WFNA): (97.5 % HNO_3, 2 % H_2O, 0-0.5 % N_2O_4)
- Red Fuming Nitric Acid (RFNA): (82-85 % HNO_3, 2-3 % H_2O, 13-15 % N_2O_4)
  - 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 N_2O_4)
- High Density: 1.52 (specific density) – best of the storable oxidizers
- Low freezing point (-41.6 C)

Kosmos – 3M

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

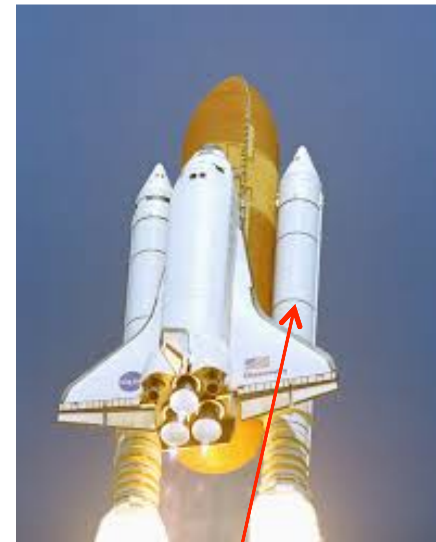
Propellants – Oxidizers

Solid Oxidizers

- Typically low energy oxidizers due to reduced mass fraction of oxidizer in the molecule

Amonium Perchlorate (NH4ClO4) (AP): [In Use]

- 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)
- Used in most solid rockets: tactical, TBM's, ICBM's, Launch vehicle propulsion
- Exhaust gases are highly corrosive and toxic (HCl acid)
- Major health issue with AP
- Cannot limit use because of the strategic importance



Space Shuttle SRB's

Propellants – Oxidizers

Amonium Nitrate (NH_4NO_3) (AN) [In Use]

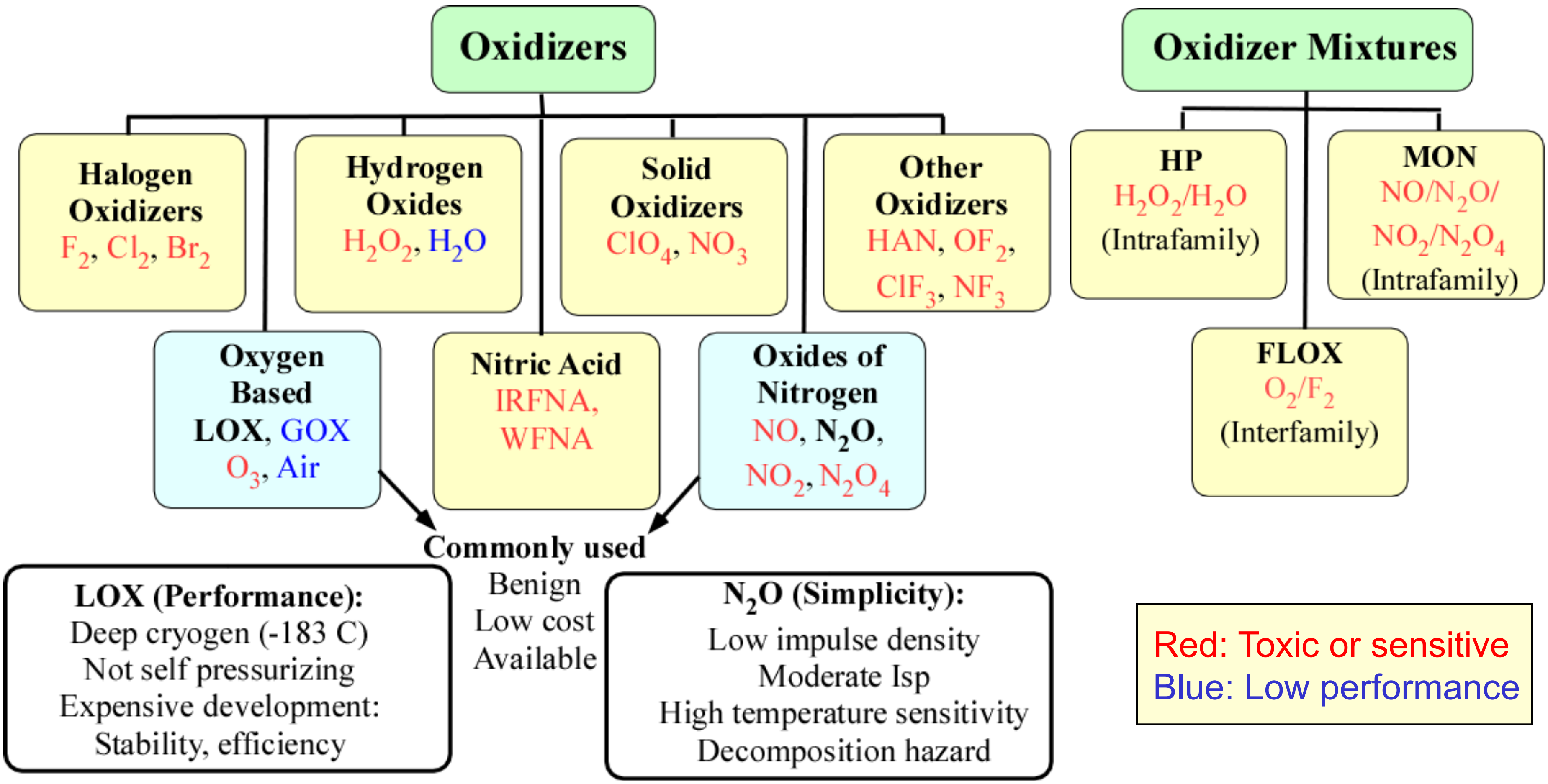
- White crystals
- Used as fertilizers
- Extremely flammable and explosive
- Low Isp compared to AP
- Specific density: 1.73
- Not used widely in the solid rocket industry
- Advantages: available, inexpensive, smokeless exhaust, nontoxic combustion products
- Solid to solid phase chance at temperatures higher than 30 C resulting in a 8 % volume change. Results in cracking
- Phase stabilized version of AN is available

Certain Tactical Systems

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



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

Propellants – Fuels

Nitrogen Containing Fuels:

Hydrazine (N_2H_4): [In Use]

- Also known as anhydrous hydrazine
- Oily hygroscopic liquid
- Hypergolic with halogens, liquid oxygen, H_2O_2 and N_2O_4
- Mixes with water
  - High Isp performance (Superior to ammonia, amines, hydrocarbons with storable oxidizers, Secondary to hydrogen): High hydrogen content and 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

UDMH ($(CH_3)_2 N_2H_2$): [In Use]

- Unsymmetrical dimethlyhydrazine
- Methyl group replaces hydrogen atom
- Lower freezing point
- Performance is slightly lower than the performance of hydrazine
- More stable than MMH

MMH ($(CH_3) NH_3$) [In Use]

- Monomethylhydrazine

Proton
Launch Vehicle

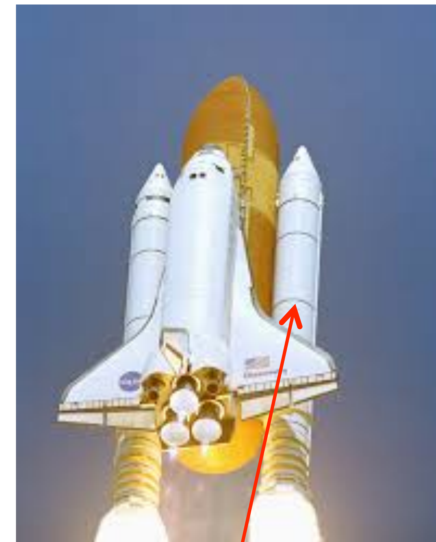
Propellants – Fuels

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): [In Use]

- 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



Space Shuttle SRB's

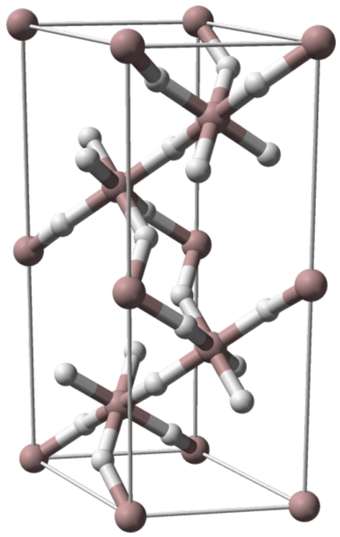
Propellants – Fuels

Beryllium (Be) [No Use]

- Extremely high energy
- Powder in crystalline phase
- Highly toxic, both acute and also chronic, carcinogenic

Metal Hydrides: [No Use]

- Combines the light weight hydrogen with the high energy metals
- Generally expensive
- In research phase
- 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



AlH3

Propellants – Fuels

Hydrogen (H_2): [In Use]

- 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): [No Use]

- 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

Space Shuttle Main Engine

Ariane V Core

Propellants – Fuels

Hydrocarbons (CnHm)

– Important source of fuels and wide range selection

Petroleum Fractions [In Use]

– 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 [In Use]

– 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)

Falcon 9
LOX/RP-1

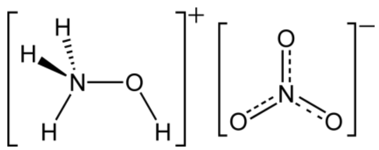
Space Shuttle SRB's

Properties of Some Liquid Fuels

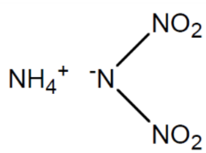
Fuel	Formula	Isp Capability	Density, g/cm3 (Temp K)	Boiling Temp, K	Melting Point, K	Corrosion	Toxicity	Shock Sensitivity
Kerosene	C10H22	High	0.8 (298)	-	230	None	Mild	Insensitive
Hydrogen	H2	Very High	0.071 (20.5)	20.39	13.96	-	None	Insensitive
Ethyl Alcohol	C2H5OH	Moderate	0.785 (298)	351.7	158.6	None	Mild	Insensitive
Hydrazine	N2H4	High	1.011(288)	386.7	274.7	Slightly	Toxic	Insensitive

Some Promising New Propellants

- Hydroxylamine Nitrate (HAN): NH3OH-NO3
  - Ionic salt
  - Oxidizing component
  - Primary use in monopropellant systems

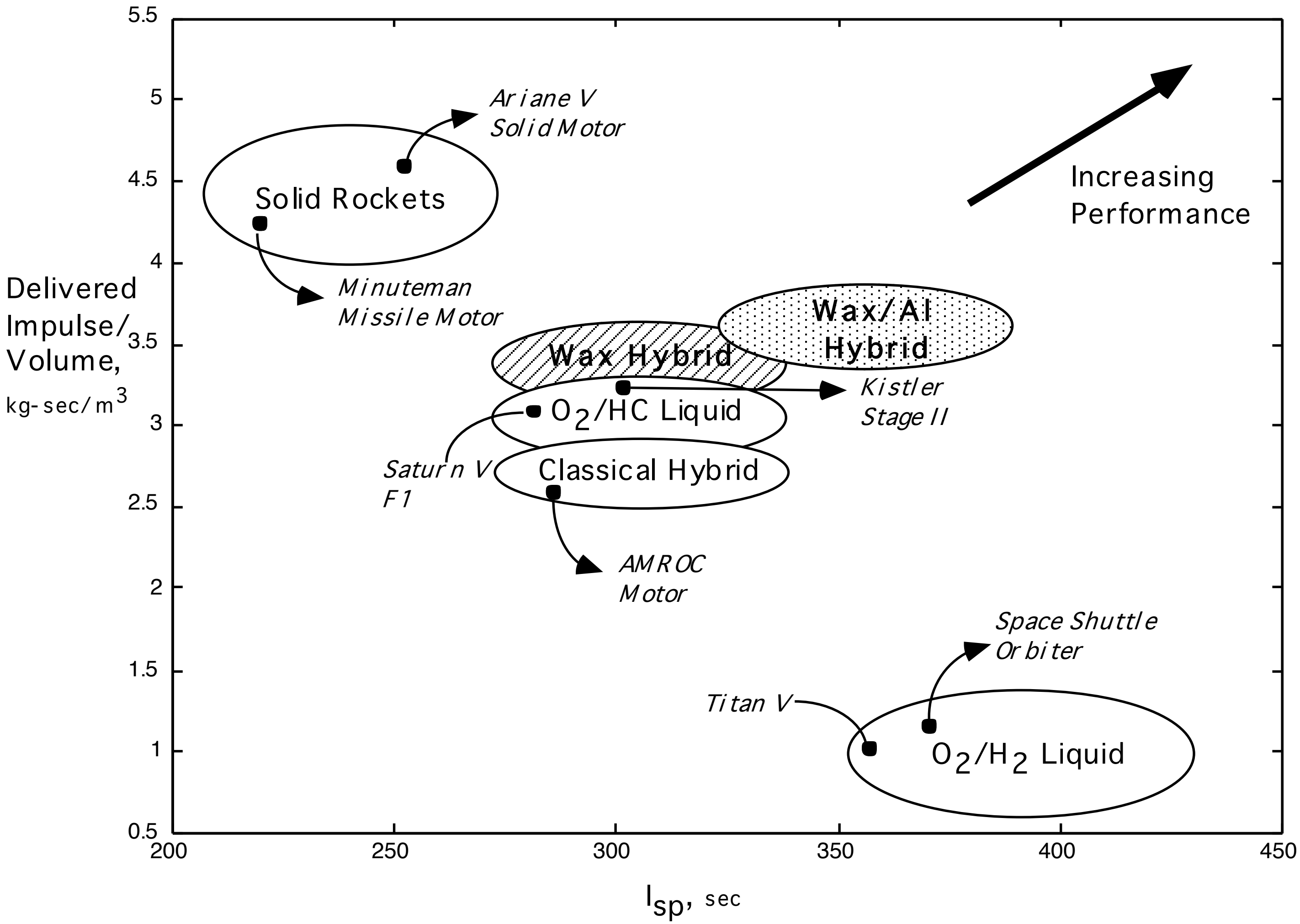


- Ammonium Dinitramide (ADN): NH4N-(NO2)2
  - Inorganic salt
  - Solid rocket oxidizer. Replacement for AP
  - Monopropellant component

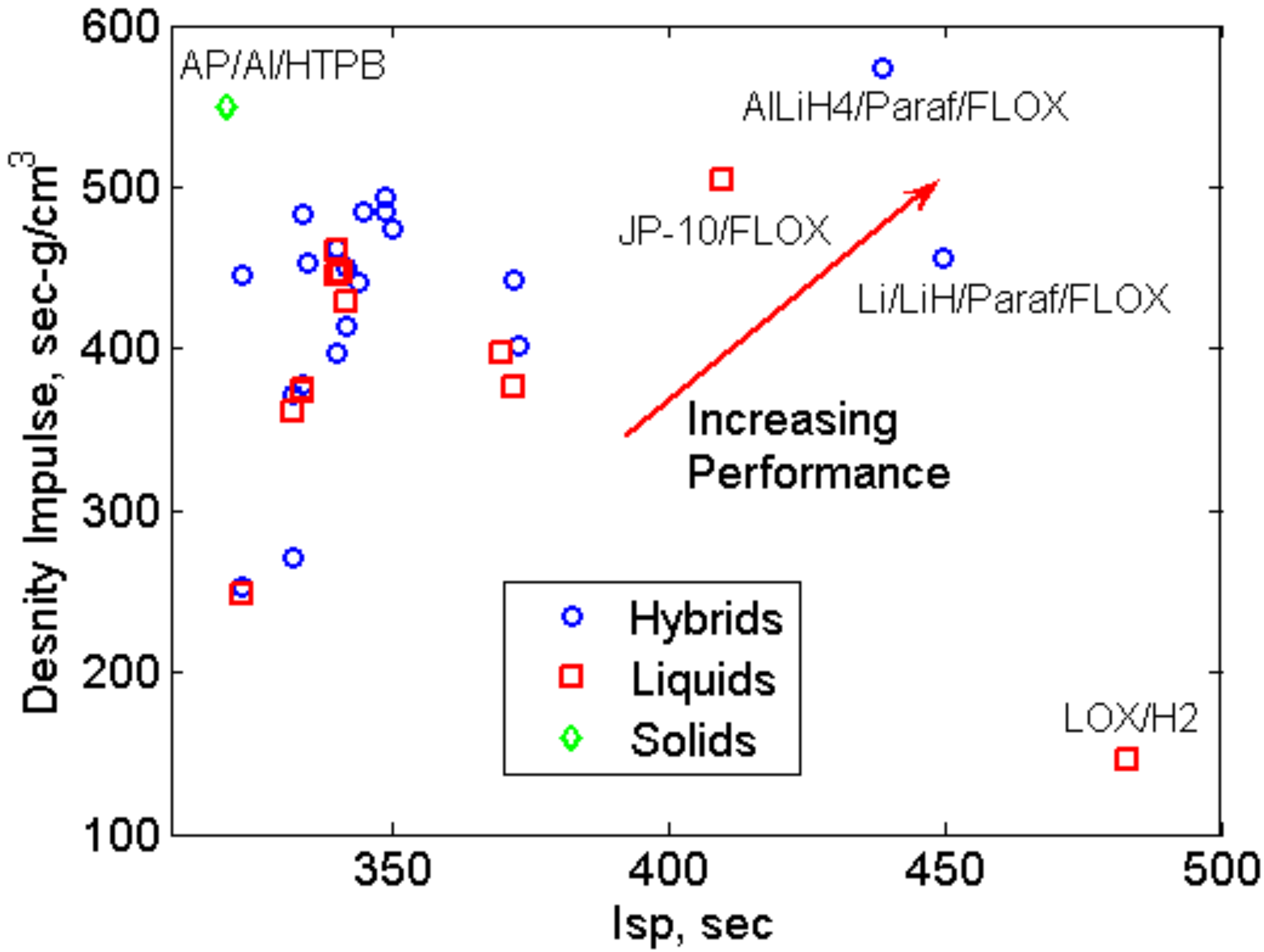


- Alane: AlH3
  - Metal hydride
  - Fuel additive for hybrid and solid rockets
  - A phase stabilized version of AlH3
  - Developed by Russians
  - Not readily available
- Alice: Water Ice/Al mixture
  - Solid rocket propellant

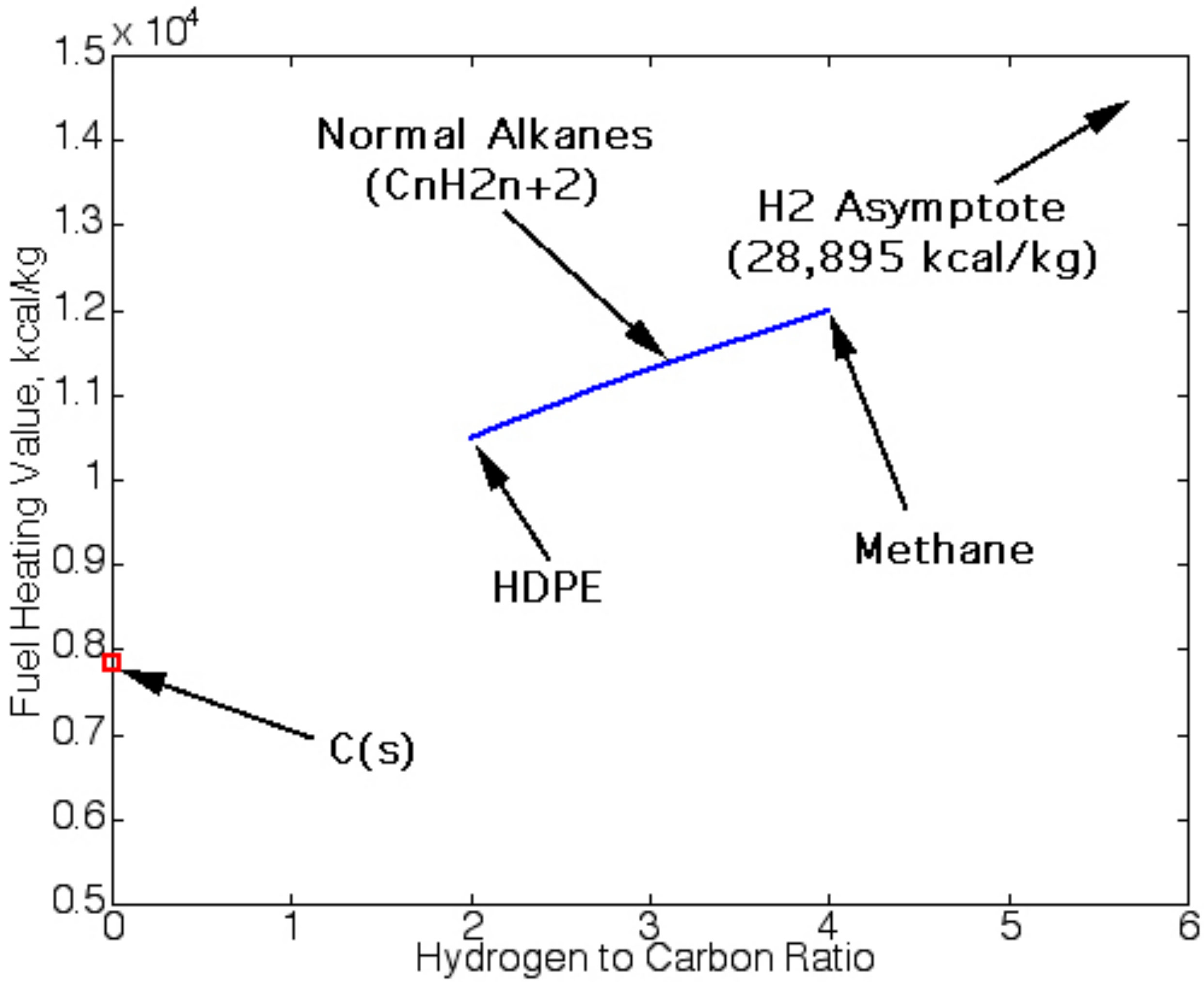
Performance of Chemical Propulsion Systems



Performance of Chemical Propulsion Systems



Heating Value of Fuels vs Hydrogen to Carbon Ratio



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