°Bachelor of Technology

Computational analysis of thermochemistry of Aluminium based propellants and ballistic properties of High-nitrogen cage compounds

A Project Report
by

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The project report entitled “Computational analysis of thermochemistry of Aluminium based propellants and ballistic properties of High-nitrogen cage compounds” submitted by Kuntumalla Gowtham (Roll No. 140100091) may be accepted for being evaluated.

Date: November 2017

Prof. Neeraj Kumbhakarna

Declaration

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Date: 21 November 2017

Abstract

This work is divided into two components. The first part is a study of kinetic, ballistic properties of High Nitrogen Cage **(HNC)** compounds which are expected to be good candidates as energetic materials for rocket propellants.

The second part consists of computer simulations of chemical reaction mechanism **(CRM)** formulated by us. It is used to validate the results of an experimental study by researchers at Texas Tech University. It follows the combustion of Teflon with Aluminium nano-particles. It is proposed that addition of certain polar solvents like Isopropanol, Acetone greatly enhances the properties of this reaction. The interaction between the thin Alumina (Al_2O_3) layer over the Al nano-particles and the solvent called the "Pre Ignition Reaction (PIR)" is proposed to be the reason behind the enhancement.

This work has the potential to disrupt how rocket propellants are conventionally prepared. The net output in terms of the thrust generated per unit mass of propellant and exothermicity greatly increase after treating the propellant mixture with certain solvents. Once proven, the sample preparation methodology can be extended to other fuel mixtures to greatly enhance efficiency.

In each chapter details of both the parts are presented one after the other. Note that the two parts of the B.Tech project will be referred to as follows.

1. **HNC** - Analysis of thermal, ballistic and detonation properties of High-nitrogen compounds
2. **CRM** - Chemical reaction mechanism formulation and theoretical validation for reaction between Aluminium nano-particles and Teflon polymer.

Keywords: High-nitrogen compounds, Preignition reaction, Teflon, Alumina, Polar solvent effect, Propulsive and Ballistic properties, Thermochemistry, Density functional Theory

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Nomenclature

T_{ad}	Adiabatic flame temperature(K)	4
Al	Aluminium	6
AlF	Aluminium Fluoride	10
Al_2O_3	Alumina	6
M_{av}	Average molecular weight of gaseous product (gm/mol)	4
ΔG	Change in Gibbs free energy	15
ΔH	Change in Enthalpy	15
ρ	Gas phase density (g/^{3})	4
g_o	Gravity at the surface of the Earth (m/s^2)	4
$\dot{m}$	Mass flow rate (kg/sec)	4
Q	Mass specific enthalpy of detonation (cal/g)	4
A_e	Nozzle exit area (m^2)	4
N	Number of moles of gaseous product per gram of explosive	4
P	Pressure (bar)	4
k_b	Backward rate constant	15
k_f	Forward rate constant	15
F	Rocket thrust force (newton)	4
I_{sp}	Specific Impulse (s)	4

ρI_{sp}	Density specific Impulse (gm.s/cm^3)	4
PTFE	Teflon (or) Polytetrafluoroethylene	6
t	Time (s)	4
$\dot{v}$	Velocity (m/s)	4
$\dot{v}$	Rate of change of Velocity (m/s^2)	4

Abbreviations

AP	Ammonium Perchlorate	14
RDX	Cyclotrimethylenetrinitramine	5
DFT	Density functional theory	2
HF	Hartree Fock Method	2
HOF	Heat of formation (kJ/mol)	4
HTPB	Hydroxyl terminated polybutadiene	14
ICE	Internal Combustion Engines laboratory	7
IRC	Intrinsic reaction coordinates	14
LOX	Liquid Oxygen	14
MDM	Melt dispersion mechanism	10
MIC	Meta stable intermolecular composite	10
MP2	Moller Plesset perturbation theory	2
PIR	Pre ignition reaction	10
RP-1	Rocket Propellant 1	14
TST	Transition state theory	10
TAGzT	Triaminoguanidinium Azotetrazolate	5

Miscellaneous Acronyms

BTP	B.Tech Project	1

CRM	Chemical reaction mechanism	1
HNC	High-nitrogen cage compound	1
NASA CEA	NASA chemical equilibrium with applications software	11

Chapter 1

Introduction

Computational analysis has grown to become a vital element of research projects these days. Preparation of reagents and chemicals is an expensive and time consuming process. Experimental setup for testing requires sufficient space, skilled manpower and robust safety procedures.

Simulation methods in the form of scientific computing software have given a novel turnaround for these issues. They are designed by organisations for specific use in research laboratories. A wide variety of software is available for many areas of interest. Specifically for research in chemistry, chemical reactions can be performed on a computer instead of test tubes!

This report comprises of results from two related projects. Finding thermal, ballistic properties of certain artificially designed "High-nitrogen Cage" compounds is the goal of the first part. Findings from analysis of reaction between Aluminium and Teflon form the second part of the project. The latter part is in progress. It will be continued in BTP- 2.

1.1 Basics

To start off, a few basic topics are discussed to give the reader a grasp of fundamental knowledge. By no means is this comprehensive. For complete details refer to Lewars (2011), McQuarrie (1997), Sanford Gordon (1994), Sanford Gordon (1996).

1.1.1 Computational Chemistry

Ab initio methods are computational chemistry methods based on quantum chemistry. Ab initio quantum chemistry methods attempt to solve the electronic Schrödinger equation given the positions of the nuclei and the number of electrons in order to yield useful information such as electron densities, energies and other properties of the system (Lewars, 2011). Basic methods are explained in more detail in section 2.2.5.

Hartree Fock (HF) methods, Moller Plesset perturbation theory (MP2) and Density functional theory (DFT) are a few examples. There is an associated accuracy with each of the theories. Usually the computational cost associated with these methods scales rapidly with increasing size(N) of the system. Some of them are as complicated as $O(\mathrm{N}^6)$.

1.1.2 Thermal properties

Heat of formation (HOF), Gas phase density (ρ) and Adiabatic flame temperature (T_{ad}) are the thermal properties of interest.

HOF :- The standard enthalpy of formation or standard heat of formation of a compound is the change of enthalpy during the formation of 1 mole of the substance from its constituent elements, with all substances in their standard states, and at a pressure of 1 bar.

ρ :- It is the density of a substance in gaseous phase. In this state a constituent molecule experiences minimum interference from surrounding molecules. It is useful to specify materialistic extent of the substance.

T_{ad} :- The constant volume adiabatic flame temperature is the temperature that results from a complete combustion process that occurs without any work, heat transfer or changes in kinetic or potential energy. The constant pressure adiabatic flame temperature is the temperature that results from a complete combustion process that occurs without any heat transfer or changes in kinetic or potential energy. Its temperature is lower than the constant volume process because some of the energy is utilized to change the volume of the system (i.e., generate work).

1.1.3 Ballistic and Detonation properties

Specific Impulse (I_{sp}) and Density specific impulse (ρI_{sp}) are the required ballistic properties. Specific impulse is a measure of how effectively a rocket uses propellant or jet engine uses fuel. By definition, it is the total impulse (or change in momentum) delivered per unit of propellant consumed and is dimensionally equivalent to the generated thrust divided by the propellant mass or weight flow rate. If mass (kilogram) is used as the unit of propellant, then specific impulse has units of velocity. If weight (newton) is used instead, then specific impulse has units of time (seconds). Multiplying flow rate by the standard gravity (g_0) converts specific impulse from the mass basis to the weight basis.

Density specific impulse is the specific impulse multiplied by density of the propellant under consideration. It takes into account the physical space propellant may occupy in the storage tank in a rocket. This quantity is useful for comparing effectiveness of different rocket propellants regardless of their individual densities.

Detonation pressure (P in kbar) and Detonation velocity (V in km/s) are the detonation properties of interest. Detonation velocity or velocity of detonation (VoD), is the velocity at which the shock wave front travels through a detonated explosive. Similarly detonation pressure is the pressure of expanding gases upstream of the shock wave. Note that the detonation properties cannot computed if Q is negative.

$$D = 15.58\rho^2 N M_{av}^{1/2} Q^{1/2}$$

$$V = 1.01\sqrt{N M_{av} Q^{1/2}}(1 + 1.13\rho)$$

where ρ (g/cm^3) is the density, M_{av} (g/mol) is the average molecular weight of the gaseous products, N (mol/g) is the number of moles of gaseous products per gram of explosive and Q (cal/g) is the mass specific enthalpy of detonation (Mallick *et al.*, 2017).

Rocket Thrust Equation:

$$F = \dot{m}V_e + (P_e - P_o)A_e$$

Equivalent Velocity:

$$V_{eq} = V_e + (P_e - P_o)A_e/\dot{m} \;\&\; F = \dot{m}V_{eq}$$

Total Impulse:

$$\begin{aligned} I &= F\Delta t \\ &= \int F dt \\ &= \int \dot{m}V_{eq} dt \\ \implies I &= mV_{eq} \end{aligned}$$

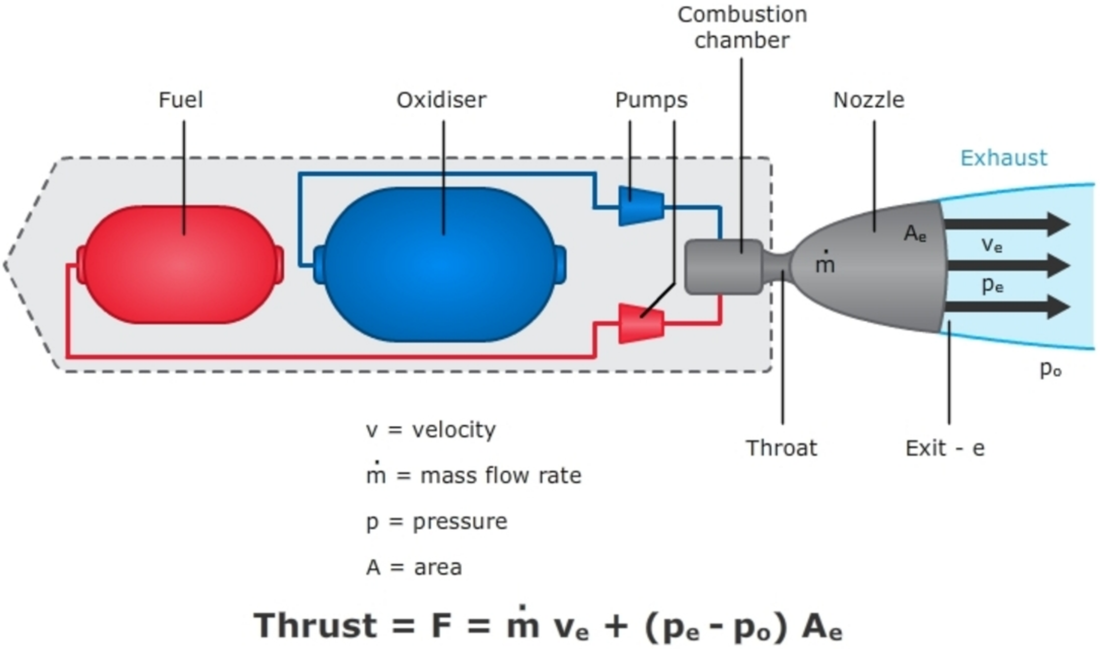


Figure 1.1: Basic rocket propulsion system

Specific Impulse:

$$I_{sp} = Total\ Impulse/Weight$$

$$= I/(mg_o)$$

$$= V_{eq}/g_o$$

$$\implies I_{sp} = F/(\dot{m}g_o)$$

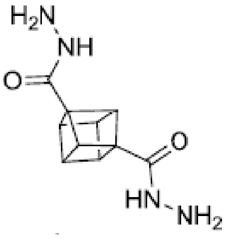
Note that the unit of I_{sp} is Second (s). This value can be compared across different propellants. Higher value of I_{sp} is desirable.

1.2 High-nitrogen cage (HNC) compounds

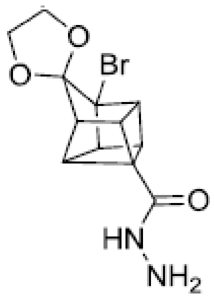
Cage hydrocarbons have been envisioned by the propellant community as suitable replacements for straight chain hydro-carbons in various high-specific-impulse and volume-limited commercial and military propulsion systems, due to their enhanced combustion characteristics over conventional propellants (Rajkumar *et al.*, 2013).

Cage compounds are characterised by three-dimensional structures which have defined rigid geometry. They are very useful synthons in organic synthesis, as well as the indispensable substrates for the mechanistic studies. Moreover, the various atomic positions in a cage can serve as branching points where the additional ligating group can be introduced. These substituted derivatives can be used as building blocks in supramolecular chemistry. The first step towards employing cage compounds in the synthesis of more complex molecular systems is the understanding of their reactions.

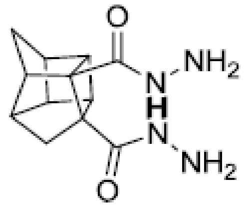
Likewise high-nitrogen cages are those 3 dimensional colsed cage compounds in which the molecular percentage of nitrogen is high. Cyclotrimethylenetrinitramine (RDX), Triaminoguanidinium Azotetrazolate (TAGzT) are two popular nitrogen rich compounds. They are well known for their superior detonation properties. Note that the above examples are not cage compounds. In this project, We explore cage compounds as shown in `table 1.1` which are envisioned to have beneficial properties theoretically.



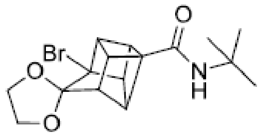
(a) HNC1



(b) HNC2



(c) HNC3



(d) HNC4

Table 1.1: High-nitrogen compounds under investigation

1.3 Aluminium, Alumina & Teflon

Aluminium (Al) is a widely used metal which finds application in numerous industries. It is the most abundant metal on planet earth. It is very reactive and very rarely found as a pure metal. Aluminium particles are naturally passivated with a 2 *to* 4 *nm* thick alumina shell that is independent of particle size (Aumann *et al.*, 1995). Because of it's crucial position alumina present on the surface plays an important role in physical and chemical properties of Al metal.

Alumina, common Al_2O_3, is highly hygroscopic in nature and can be used as adsorbent and desiccating agent. In atmosphere, it forms a thin outer crust of aluminium oxide which is stable. Also this thin layer prevents further production of oxide passivisation layers. Reaction of aluminium (as it is a reducing agent) with oxidising agents like ammonium perchlorate, Polytetrafluoroethylene (PTFE) releases large amount of energy and byproducts. In fact, this reaction is used in the solid rocket booster as the solid rocket propellant for providing about 75% of thrust required to lift off a space launch system.

Teflon (®DuPont) *aka* PTFE is a white, highly hydrophobic solid polymer which is neutral at normal atmospheric conditions and does not react directly at room temperatures. In fact, Teflon is used as non-stick coating for heating pans and utensils. Melting point of Teflon is around 327°C and decomposes into small chains at around 350°C. At higher temperatures it breaks down into highly reactive Florine species which are powerful oxidising agents. Reactions between Al, Al_2O_3 and all these species are of interest.

Chapter 2

Literature Survey

2.1 Research collaboration

The Chemistry department at IIT Bombay has ties with Internal Combustion Engines (ICE) laboratory. The necessary computational background and framework is available in the ICE lab. Molecules are designed theoretically by ICE and are analytically simulated in the software mentioned later. If the results obtained are satisfactory these chemicals move forward to next stage in production planning in the chemistry lab. HNC compounds are few such strained cage molecules which are under intense study in recent times. Molecules mentioned in 1.1 were selected as good candidates for research after initial analysis.

2.2 Aluminium particle combustion in CRM

2.2.1 How we came about this topic

Researchers at the Texas tech University in Lubbock, Texas, USA have been actively working on experiments related to aluminium based propellants. Solvents used for preparing experimental samples had effect on the propellant properties such as flame speed and specific impulses. An article by Padhye *et al.* (2015) was the one which raised this interesting issue by testing it experimentally. In later articles, the same researchers Padhye *et al.* (2016), Padhye *et al.* (2017) tried to propose plausible explanations. These explanations lack a comprehensive reaction mechanism solution which can concretely establish the results observed experimentally. Losada and Chaudhuri (2009) have tried approaching this problem but haven't quite finished it. This project is an attempt in this direction.

2.2.2 Reaction mixture preparation

To set the stage for further discussion, it is important to clearly mention the method employed by the aforementioned researchers Padhye *et al.* (2015). The following paragraph has been taken verbatim from the above articles with minor edits. This has been done so as to not lose originality

“For reactivity studies, Al and PTFE powders were combined to give a mixture of 40 wt % Al with PTFE. This composition, which corresponds to an Al:PTFE equivalence ratio of 1.5, has been shown to be optimal for producing high flame speeds. To ensure good dispersion, the Al and PTFE powders were suspended in solvent (1.0 g of solid in 60 mL of solvent) and sonicated at 600 W for 60 s, using a programmed cycle of 10 s on and 10 s off. Afterwards, an aliquot of solution was poured into a shallow Pyrex dish that was placed in a fume hood, and the dried mixture (Al + PTFE) was reclaimed following solvent evaporation. Scanning electron microscopy (SEM) techniques were used to assess the uniformity of mixing between Al and PTFE phases in Al + PTFE samples. It shows the dispersion of phases is typical for organic solvent dispersed Al + PTFE thermite mixtures and indicates differences in the physical mixing among samples should not significantly influence the variations in reactivity reported.”

We observe that the solvent used for dispersion would still be present in the final reaction mixture. This is because fume hood evaporation is not strong enough to remove all of the solvent content completely. Some of it would be bonded to thermite either physically or chemically.

2.2.3 The effect of solvent on reactivity

We are out to prove if the addition of solvent during preparation (Padhye *et al.*, 2015) of Al (surrounded by Al_2O_3) + PTFE mono propellant mixture is actually chemically beneficial. We are concerned with the energies of chemical reactions involved in this process. Quantifying this effect is the crux of this study. Physical constraints like contact surface between aluminium sphere particles and PTFE are not considered.They are assumed to meet ideal requirements.

The Al+PTFE mixture can be termed as a “metastable intermolecular composite” (MIC) because these mixtures are of higher energy than the decomposition products but sufficiently stable under ambient conditions. Also they are highly exothermic (Losada and Chaudhuri, 2009).

This paper (Padhye *et al.*, 2015) implies that polar solvents may facilitate more complete combustion and enhanced reactivity via added chemical energy that is liberated upon reactions of alumina shell surface with fluorine. They performed DSC (Differential scanning calorimetry) experiments with polar and nonpolar solvents viz.2-Propanol, Acetone (both are polar) and Hexane (Nonpolar). A glance at the bond energies of respective atomic level bonds shows us why the reaction is feasible and so energetic. *Appendix A* summarises the approximate values of important bond strengths.

2.2.4 Melt Dispersion Mechanism

Considering basic chemical interactions between different molecules and looking at the available literature following theories were proposed. Melt Dispersion Mechanism (MDM) (Mulamba and Pantoya, 2014) is a very convincing theory which explains the surface effects of thermite on top of core Al nanoparticles.

MDM is a multi-stage process beginning with the melting of Al core which causes an increase in volume. This volume increment is associated by an rapid increase in pressures upto $1 - 3\ GPa$ (Levitas *et al.*, 2008) and tensile hoop stress in the oxide shell of up to 10 GPa. This hoop stress causes fast fracture and spallation of the shell. The exposed molten Al surface leads to a pressure gradient that creates an unloading wave dispersing small Al droplets in all directions. This results in a very high reaction rates between any compound surrounding the nanoparticle.

Preignition reaction (PIR) is a reaction between fluorine radicals and "*type 1a hydroxyl*" ions (Sarbak, 1997) in Al_2O_3. Stable AlF_3 is a product which releases energy. Simply said PIR improves the stability of Al_2O_3 passivation shell by adding an extra layer of AlF on top of it. Stronger outer shell implies higher stresses which result in even stronger unloading waves. This leads to improved effectiveness of MDM.

It is prudent to mention that the perceived effect of PIR is visible only in nanoscale mixtures and absent in micron scale (Osbone and Pantoya, 2007). This is attributed to various reasons such as requirement of sufficient surface area to volume ratio for good contact and incomplete decomposition of PTFE in those conditions.

Polar solvents introduce more hydroxyl ions (OH^-) in alumina shell which thereby facilitates substitution by fluorine radicals in fuel/oxidiser mixture during the heating. This leads to more stable coating of Al-F on Al_2O_3 hence stronger shell which leads to larger combustion energy and faster reaction kinetics. Padhye *et al.* (2017) mention that crystalline Al_2O_3 has better exothermicity and flame speeds than amorphous type.

2.2.5 Computational techniques

There are various molecular modelling techniques (Lewars, 2011). The main tools available belong to five broad classes as described below.

- Molecular Mechanics (MM)
- *ab initio* methods
- Semiempirical (SE) methods
- Density functional (DFT) calculations
- Molecular Dynamics (MD)

Among them Molecular Mechanics methods are usually simple in the sense that they assume molecules to be hard spheres and are connected together by springs. SE, *ab initio* and DFT methods are based on Schrödinger equation.

Density functional calculations are usually faster than ab initio, but slower than SE. DFT is relatively new. Serious DFT computational chemistry goes back to the 1980's, while computational chemistry with the ab initio and SE approaches was being done in 1960s.

Heat of formation can be calculated in many different procedures. To maintain uniformity method mentioned in Osmont *et al.* (2007) is used. Refer to Ochterski (2000) for understanding how to use output from Gaussian `*.log` file. Using NASA CEA, propulsive properties are calculated as elucidated in Mallick *et al.* (2017). Mentioned software is elaborated in the next section 3.1.

In a reaction, Classical Transition State Theory (TST) is used to find the thermal properties such as heats of reaction as Enthalpy, Gibbs Free Energy of the reaction, Transition state energy.

Chapter 3

Simulation Methods

3.1 Software

In this study, Gaussian 09 suite of programs are utilised for molecular modelling and reaction simulations. Density functional theory/ab initio level quantum mechanics based methods in computational chemistry are used for simulations.

Kinetic rate constants are found out using classical transition state theory (TST).It is a popular theory well established over many decades (Truhlar *et al.*, 1996) (Laidler and King, 1983). Wigner tunnelling is used to account for possible quantum tunnelling in the chemical reactions.

NASA CEA (chemical equilibrium with applications) is used for finding propulsive properties such as adiabatic flame temperature, specific impulse and density specific impulse. These values are further utilised to get the ballistic properties using equations mentioned earlier 1.1.3.

3.2 Formal methodology employed for simulations

A preset bunch of procedures are adopted to streamline and ease the process of analysing the bulk of data.

3.2.1 Framework for HNC simulations

The following steps were formulated for analysing a given molecule. Methods for other molecules follow suit with minor variations.

1. Firstly in the GaussView software, design the given molecule roughly and `clean` it. Create a `*.com` type file.

2. Optimise the individual molecules using code which is similar to the following. These edits are done in the `*.com` file formed above using any text editor.

   ```
   \\ START (remove in actual code)
   %nprocshared=4
   %mem=4GB
   %chk=highnitrogencomp11.chk
   # opt=(tight,maxcycle=100) freq b3lyp/6-311++g(d,p) nosymm
   geom=connectivity int=grid=ultrafine

   highnitrogencomp11


   ......
   ....
   \\ END  (remove in actual code)
   \\ NOTE: these dots represent the spatial coordinates of
   \\ atoms and Z-matrix. Check Gaussian manual to get more info.
   ```

   Explanation :- The above code is for a molecule named `highnitrogencomp11` also referred to as HNC1 here. The level of density functional theory used for optimisation and frequency calculation is `b3lyp/6-311++(d,p)`. `freq` is a keyword used for finding thermochemistry of the molecule. It is performed only after the optimised molecular structure is found. `nosymm` keyword is added to ignore symmetric solution pathway in the solver. A `*.chk` is a checkpoint file which contains useful data for restarting aborted runs.

3. After sufficient amount of time, look at the `*.log` file and search for `Normal termination` at the end of the file. If successfully terminated go forward and take the following values in the thermochemistry section.

   (a) Zero-point correction= 0.220576 (Hartree/Particle)
   (b) Thermal correction to Energy= 0.235219
   (c) Thermal correction to Enthalpy= 0.236163

(d) Thermal correction to Gibbs Free Energy= 0.176524

(e) Sum of electronic and zero-point Energies= -757.509284

(f) Sum of electronic and thermal Energies= -757.494641

(g) Sum of electronic and thermal Enthalpies= -757.493697

(h) Sum of electronic and thermal Free Energies= -757.553336

Explanation :- These values are actual values obtained for the molecule HNC1 (1.1a) by running the above code. They are used for computation of HOF using theory mentioned before in section 2.2. Unit of energy is “Hartree/ Particle” or molecule.

```
1 Hartree = 27.2114 eV
1 Hartree = 627.509 kcal/mol
```

4. Next, compute the density using following code. The code is used to obtain molecular volume. Molecular mass is calculated manually. Hence gas phase density can be obtained by dividing molecular mass by volume. Density is used in further calculations.

```
\\START (remove in actual code)
%nprocshared=4
%oldchk=highnitrogencomp11.chk
%mem=4GB
%chk=highnitrogencomp11_vol.chk
# geom=allcheck Volume

highnitrogencomp11
\\END (remove in actual code)
```

5. NASA CEA is used to compute the propulsive properties mentioned above. Refer to the NASA CEA manual for appropriate settings. Procedure used in the article Mallick *et al.* (2017) is used here. Refer to Sanford Gordon (1994) and Sanford Gordon (1996) for clear steps. Heat of formation in *kcal/mol* and gas phase density, ρ in *gm/cm3* are manually entered in the software for each molecule.

6. Following are the different types of propulsion mixture combinations for which properties are calculated.AP is Ammonium Perchlorate. HTPB is hydroxyl terminated polybutadiene. LOX is liquid Oxygen. RP-1 is “Rocket Propellant-1” commonly used in launch vehicle rockets.
    (a) Performance as Solid Bipropellant with AP as oxidizer (20% HNC, 80% AP)
    (b) Performance as additive to AP-HTPB mixture (80% AP, 15% HTPB, 5% HNC)
    (c) Performance as propellant with LOX as oxidizer
    (d) Performance as additive to RP-1 with LOX as oxidizer
    (e) Performance as Monopropellant
7. The results of propulsive properties are tabulated in the results section. Detonation properties are calculated if Q is +ve and tabulated separately.

3.2.2 Methodology for CRM

In the chemical reaction mechanism formulation, only Gaussian software is used. Here in we optimise the electronic structures of the molecules and simulate the reaction as follows.

1. Basic reactants, products optimisation + `freq` using `CBSQB3` theory
2. `Scan` calculation to find Transition State (TS) of the reaction using simple theory
3. Transition State optimisation using same simple theory
4. Perform `IRC` (Intrinsic Reaction Coordinate) calculations for both forward & backward iterations starting from the transition state.
5. Transition State(TS) optimisation using CBSQB3 theory, which is a high level theory.
6. Find the kinetics, thermochemical parameters (activation energies, ΔG,ΔH, k_f,k_b etc) using transition state theory mentioned earlier.

Explanation :- IRC is done to verify the correctness of the transition state. This formal methodology has been tested and verified using the following exothermic reaction.

$$N_2H_4 + NO_2 \longrightarrow N_2H_3 + HONO$$

The following terminology is used frequently.

$$\Delta H = Change\ in\ Enthalpy$$

$$\Delta G = Change\ in\ Gibbs\ free\ energy$$

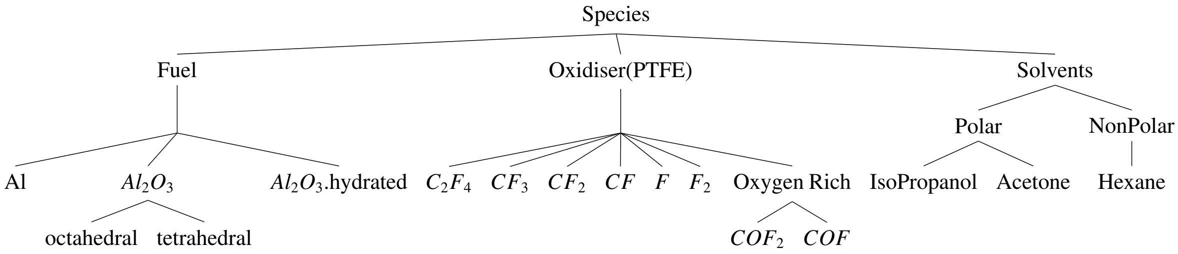
$$k_f = Forward\ rate\ constant$$

$$k_b = Backward\ rate\ constant$$

A transition state is a first order saddle point on a potential energy surface (PES). The vibrational spectrum of a transition state is characterized by one imaginary frequency (implying a negative force constant), which means that in one direction in nuclear configuration space the energy has a maximum, while in all other (orthogonal) directions the energy is a minimum. This has to be established after every TS calculation to ensure correctness.

3.3 Chemical Reaction Mechanism - CRM

The expected interacting species are mentioned in the table 3.3.



3.3.1 Reactions between PTFE decomposition species and different Al species

The following reaction mechanism has been formulated after looking at earlier articles (Losada and Chaudhuri, 2009), (Padhye *et al.*, 2016). General reactions are categorised under one of the following types.

- Al_2O_3-OH + fluorine containing radical –> Al_2O_3-F + OH^- + Other Products
  Note: This may occur with and without solvent

- Solvent + fluorine containing radical –> fluorine substituted solvent.
  Note: This occurs specifically with the presence of solvent. Solvent may act as carrier to the fast moving and highly reactive fluoride radicals.

- Al_2O_3-OH + fluorine substituted solvent –> Al_2O_3-F + Solvent
- Solvent –> Decomposition products

Chapter 4

Results and Discussions

4.1 Properties of High-nitrogen cage (HNC) compounds

4.1.1 Summary of results

Results of the simulations are presented in the following tables. Table 4.1 gives heat of formation and gas phase density obtained from Gaussian simulations. Tables 4.2, 4.3, 4.4, 4.5, 4.6 give the propulsive properties in various operating conditions as obtained from NASA CEA calculations. Table 4.7 gives the detonation properties of all the molecules. These results were submitted to Prof. I N N Namboothiri of Chemistry department for perusal.

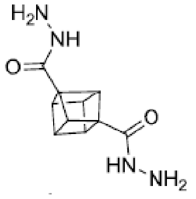
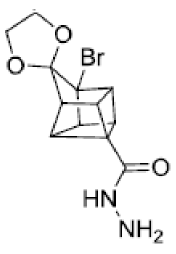
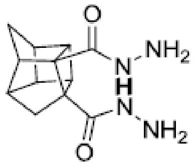
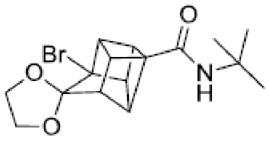
4.1.2 Observations on Heat of Formation

Coming to table 4.1, we see that molecule 1 i.e. HNC1 has high heat of formation. It may be unstable because of the highly strained structure of base Cubane cage. This is supported by the decrements in the scalar value of HOF of other compounds. HNC2 has 9 carbon atoms in the cage whereas HNC3, HNC4 have 10 carbon atoms each. The external chains, rings probably do not affect the stability too much. But they do play an important role in chemical reactions because of high steric hindrance.

4.1.3 Remarks on propulsive properties

Different types of conditions are employed for simulating and finding the expected propulsive properties of the given compounds. Specific Impulse I_{sp} and it's density variant are the most important properties to consider when comparing effectiveness of rocket propellants. It is a measure of how effectively a rocket uses propellant or jet engine

Table 4.1: Molecular Structure[a] of HNC compounds and Heat of Formation

Notation	Formula	Molecular structure	Heat of Formation ($kcal/mol$)	Density, ρ (gm/cm^3)
HNC1	$C_{10}H_{12}N_4O_2$		151.39	1.558
HNC2	$C_{12}H_{13}N_2O_3Br$		82.64	1.80
HNC3	$C_{12}H_{16}N_4O_2$		69.2	1.48
HNC4	$C_{16}H_{20}NO_3Br$		43.46	1.58

a: Optimisation done using B3LYP density function theory with 6-311++G(d,p) basis set

uses fuel.

In 4.2 all the HNC compound act as fuel in a solid state mixture. The results indicate that the effectiveness decreases in linear order. In 4.7 we observe that heavier molecules with heavy atoms such as Bromine tend to have lower values of detonation properties. This arises from a calculation procedure where we assume Br does not directly participate in detonation reaction.

Table 4.8 has been obtained from Mallick *et al.* (2017) for reference. The compounds mentioned are commonly used as propellants in rockets. Available data is presented in it's standard form. We observe that the molecules we chose indeed have better specific impulse. Density specific impulse is observed to be only marginally (around 10 $g.sec/cm^3$)

Table 4.2: Performance as Solid Bipropellant with AP as oxidizer (20% HNC, 80% AP)

Compound	CCT(K)	I_{sp} (s)	$I_{sp,vac}$ (s)
$C_{10}H_{12}N_4O_2$	3183.92	300.31	311.32
$C_{12}H_{13}N_2O_3Br$	3095.82	290.85	302.69
$C_{12}H_{16}N_4O_2$	3048.91	290.9	301.10
$C_{16}H_{20}NO_3Br$	3076.49	287.94	298.4

Here CCT is Combustion chamber temperature, same as Adiabatic temperature mentioned in previous chapters.
AP: Ammonium Perchlorate, I_{sp}: Specific Impulse, $I_{sp,vac}$: I_{sp} in Vacuum conditions

Table 4.3: Performance as additive to AP-HTPB mixture (80% AP, 15% HTPB, 5%HNC)

Compound	CCT(K)	I_{sp} (s)	$I_{sp,vac}(s)$
$C_{10}H_{12}N_4O_2$	2609.44	274.07	284.01
$C_{12}H_{13}N_2O_3Br$	2622.49	272.56	282.36
$C_{12}H_{16}N_4O_2$	2542.2	271.02	281.01
$C_{16}H_{20}NO_3Br$	2561.34	270.51	280.43

Here CCT is Combustion chamber temperature, same as Adiabatic temperature mentioned in previous chapters.
AP: Ammonium Perchlorate, HTPB: Hydroxyl-terminated polybutadiene
I_{sp}: Specific Impulse, $I_{sp,vac}$: I_{sp} in Vacuum conditions

larger than the common compounds. Nonetheless even small improvements in these properties have huge impacts.

Thus this theoretical study establishes HNC candidates as suitable candidates to replace conventional rocket fuels. The ability to bring these propellants to reality depends on the ease of preparation of constituent molecules and ultimately the price economics.

4.2 CRM: Does it work?

This is still an ongoing effort. Results will be delivered after sufficient number of simulations are performed and proved.

4.2.1 Discussions on proposed reaction mechanism

The main motive of conducting this study is to identify and verify with certainty the enhancing effect of solvents on propellants. Researchers have experimentally observed positive increase (nearly twice) in exothermicity and flame speeds. In general, the following is the expected impact.

Table 4.4: Performance as propellant with LOX as oxidizer

Compound	O/F Ratio	CCT(K)	Ratio $\sqrt{T_{ad}/MW}$	I_{sp} (s)	$I_{sp,vac}$ (s)	ρI_{sp} $(gm.s/cm3)$	$\rho I_{sp,vac}$ $(gm.s/cm3)$
$C_{10}H_{12}N_4O_2$	1.14	3861.76	12.15	352.40	366.73	459.53	478.22
$C_{12}H_{13}N_2O_3Br$	1	3783.29	11.62	300.39	309.46	419.95	432.63
$C_{12}H_{16}N_4O_2$	1.38	3752.51	11.82	344.85	359.40	434.81	453.15
$C_{16}H_{20}NO_3Br$	1.28	3756.37	11.22	331.72	346.61	430.99	450.33

Here CCT is Combustion chamber temperature, same as Adiabatic temperature (T_{ad}) mentioned in previous chapters.
O/F: Oxygen to Fuel ratio. MW: Molecular Weight of compound
I_{sp}: Specific Impulse, $I_{sp,vac}$: I_{sp} in Vacuum conditions, ρI_{sp} Density specific Impulse

Table 4.5: Performance as additive to RP-1 with LOX as oxidizer (30% HNC, 70% RP-1)

Compound	O/F Ratio	CCT(K)	Ratio $\sqrt{T_{ad}/MW}$	I_{sp} (s)	$I_{sp,vac}$ (s)	ρI_{sp} $(gm.s/cm3)$	$\rho I_{sp,vac}$ $(gm.s/cm3)$
$C_{10}H_{12}N_4O_2$	2.15	3698.2	12.04	350.97	365.96	387.49	404.05
$C_{12}H_{13}N_2O_3Br$	2.11	3683.95	11.83	346.16	391.02	391.02	441.69
$C_{12}H_{16}N_4O_2$	2.22	3680.23	11.98	349.36	382.83	382.83	419.52
$C_{16}H_{20}NO_3Br$	2.19	3682.27	11.86	346.77	383.83	383.83	424.85

Here CCT is Combustion chamber temperature, same as Adiabatic temperature (T_{ad}) mentioned in previous chapters.
RP1: Rocket Propellant 1, O/F: Oxygen to Fuel ratio. MW: Molecular Weight of compound
I_{sp}: Specific Impulse, $I_{sp,vac}$: I_{sp} in Vacuum conditions, ρI_{sp} Density specific Impulse

$$Polar\ solvents > Non-polar\ solvents > No\ solvation$$

As discussed earlier there are multiple reaction pathways possible. The formation of Al-F bond on top of Al-Al_2O_3 sphere is believed to be the reason for this enhancement. Melt dispersion mechanism is perceived to be a driving factor behind this. And PIR enhances the effectivity of MDM. This section will be further updated after finding a working solution.

4.3 Future work

As mentioned earlier, the second part of the project i.e. the work on the reaction mechanism formulation is still underway. Only a rough reaction mechanism based on intuition has been proposed. It has to be validated through computer simulations on Gaussian. This will be taken up in BTP-2.

Table 4.6: Performance as Mono-propellant

Compound	CCT(K)	Ratio $\sqrt{T_{ad}/MW}$	I_{sp} (s)	$I_{sp,vac}$ (s)	ρI_{sp} $(gm.s/cm3)$	$\rho I_{sp,vac}$ $(gm.s/cm3)$
$C_{10}H_{12}N_4O_2$	2044.95	12.82	260.32	272.29	405.51	424.17
$C_{12}H_{13}N_2O_3Br$	1701.93	10.32	209.24	219.83	377.57	396.68
$C_{12}H_{16}N_4O_2$	1417.65	10.74	219.54	230.90	323.74	340.48
$C_{16}H_{20}NO_3Br$	1378.49	9.89	195.07	205.55	308.15	324.71

Here CCT is Combustion chamber temperature, same as Adiabatic temperature (T_{ad}) mentioned in previous chapters.

O/F: Oxygen to Fuel ratio. MW: Molecular Weight of compound

I_{sp}: Specific Impulse, $I_{sp,vac}$: I_{sp} in Vacuum conditions, ρI_{sp} Density specific Impulse

Table 4.7: Predicted detonation properties

Compound	Detonation Pressure ($kBar$)	Detonation Velocity (Km/s)
$C_{10}H_{12}N_4O_2$	132.74	5.69
$C_{12}H_{13}N_2O_3Br$	104.8	4.86
$C_{12}H_{16}N_4O_2$	215.99	7.43
$C_{16}H_{20}NO_3Br$	77.92	4.36

Note: for some compounds Q becomes negative and these properties cannot be calculated using this method in those cases

Table 4.8: Propulsive properties of currently used compounds

Compound	Compound + LOX		Compound (30%)+ RP1 (70%)+LOX		As monopropellant	
	I_{sp}	$\rho I_{sp,vac}$	I_{sp}	$\rho I_{sp,vac}$	$I_{sp,vac}$	$\rho I_{sp,vac}$
$RP1$	366.2	374.3	-	-	-	-
N_2H_4	-	-	-	-	234.1	235.3
IPN	-	-	-	-	251.6	261.7

N_2H_4 is Hydrazine. isopropyl nitrate (IPN, $(CH_3)_2CHONO_2$).

I_{sp} is in seconds. $\rho I_{sp,vac}$ is in $gm.s/cm3$

Appendix A

Bond Energies

Scission of C-C bonds (348 kJ/mol) takes place because of its weaker strength compared to C-F bond (507 kJ/mol). Similarly, Al-F bond is stronger (675 kJ/mol) than either of these two at 298K. Also Al-O bond strength is around 501.9 kJ/mol. Bond strength of C-O is about 1076.4 kJ/mol. The following values are obtained from Luo (2007).

Bond strength D°_{298} kJ/mol at 298K	H	C	O	F	Al
H	432	413	467	565	288
C	-	346(sigl)	358(sigl)	485	567.7
O	-	-	146	190(sigl)	501.9(sigl)
F	-	-	-	154	675
Al	-	-	-	-	264.3

References

Aumann, C. E., Skofronick, G. L., and Martin, J. A., 1995, “Oxidation behavior of aluminum nanopowders,” *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **13**, 1178–1183.

Laidler, K. J., and King, M. C., 1983, “Development of transition-state theory,” *The Journal of Physical Chemistry* **87**, 2657–2664.

Levitas, V. I., Pantoya, M. L., and Watson, K. W., 2008, “Melt-dispersion mechanism for fast reaction of aluminum particles: Extension for micron scale particles and fluorination,” *Applied Physics Letters* **92**, 201917.

Lewars, E. G., 2011, *Computational Chemistry* (Springer Netherlands).

Losada, M., and Chaudhuri, S., 2009, “Theoretical study of elementary steps in the reactions between aluminum and teflon fragments under combustive environments,” *The Journal of Physical Chemistry A* **113**, 5933–5941.

Luo, Y. R., 2007, *Comprehensive Handbook of Chemical Bond Energies* (CRC Press, Boca Raton, FL).

Mallick, L., Lal, S., Reshmi, S., Namboothiri, I. N. N., Chowdhury, A., and Kumbhakarna, N., 2017, “Theoretical studies on the propulsive and explosive performance of strained polycyclic cage compounds,” *New J. Chem.* **41**, 920–930.

McQuarrie, D. A., 1997, *Physical chemistry: a molecular approach* (Sausalito, Calif.: University Science Books).

Mulamba, O., and Pantoya, M. L., 2014, “Exothermic surface chemistry on aluminum particles promoting reactivity,” *Applied Surface Science* **315**, 90 – 94.

Ochterski, J. W., 2000, “Thermochemistry in gaussian,” `http://gaussian.com/thermo/`, Accessed: 2017-11-07.

Osbone, D. T., and Pantoya, M. L., 2007, "Effect of al particle size on the thermal degradation of al/teflon mixtures," *Combustion Science and Technology* **179**, 1467–1480.

Osmont, A., Catoire, L., Gokalp, I., and Yang, V., 2007, "Ab initio quantum chemical predictions of enthalpies of formation, heat capacities, and entropies of gas-phase energetic compounds," *Combustion and Flame* **151**, 262 – 273.

Padhye, R., Aquino, A. J. A., Tunega, D., and Pantoya, M. L., 2016, "Effect of polar environments on the aluminum oxide shell surrounding aluminum particles: Simulations of surface hydroxyl bonding and charge," *ACS Applied Materials & Interfaces* **8**, 13926–13933.

Padhye, R., Aquino, A. J. A., Tunega, D., and Pantoya, M. L., 2017, "Fluorination of an alumina surface: Modeling aluminum fluorine reaction mechanisms," *ACS Applied Materials & Interfaces* **9**, 24290–24297.

Padhye, R., McCollum, J., Korzeniewski, C., and Pantoya, M. L., 2015, "Examining hydroxyl alumina bonding toward aluminum nanoparticle reactivity," *The Journal of Physical Chemistry C* **119**, 26547–26553.

Rajkumar, S., Choudhari, R. S., Chowdhury, A., and Namboothiri, I. N., 2013, "Synthesis and pyrolysis studies of bis(nitratomethyl)-1,3-bishomocubane- a high-energy high-density liquid," *Thermochimica Acta* **563**, 38 – 45.

Sanford Gordon, B. J. M., 1994, "Computer program for calculation of complex chemical equilibrium compositions and applications i. analysis,"

Sanford Gordon, B. J. M., 1996, "Computer program for calculation of complex chemical equilibrium compositions and applications ii. user's manual and program description,"

Sarbak, Z., 1997, "The effect of fluoride concentration and catalyst preparation method on structural and thermal properties of como/al2o3 catalysts," *Crystal Research and Technology* **32**, 1007–1013.

Truhlar, D. G., Garrett, B. C., and Klippenstein, S. J., 1996, "Current status of transition-state theory," *The Journal of Physical Chemistry* **100**, 12771–12800.

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