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

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Introduction

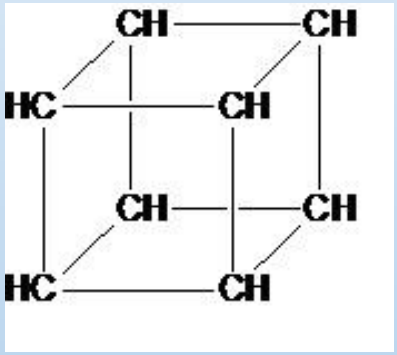
- Two Projects
  1. **HNC** - High-nitrogen cage compounds analysis (Dec 2016 - Jan2017)
     - ✓ Computational analysis of ballistic and detonation properties
     - ✓ Better propellants in terms of Specific Impulse (I_{sp}) ?
  2. **CRM** – Aluminium Nano-particles and Teflon polymer reaction (Jul 2017 – Dec 2017)
     - ✓ Formulation of chemical reaction mechanism (CRM)
     - ✓ Theoretical validation of mechanism
     - ✓ Effect of solvents on reaction

Topic 1

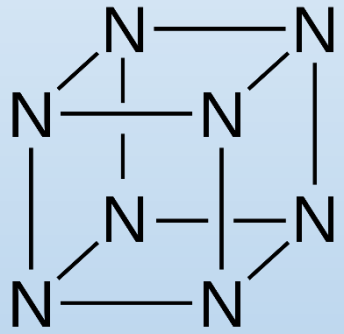
High-nitrogen cage compounds (HNC)

Literature Review - HNC

- It is a research collaboration between chemistry department and mechanical department of IITB.
- Look at the analogy



Cubane (solid)

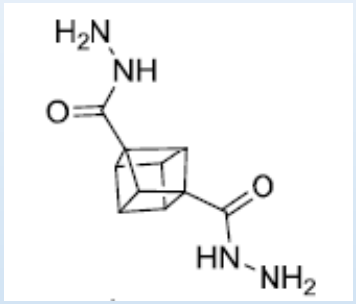


Octazacubane

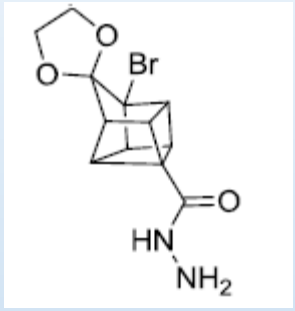
Cage compounds with carbon majority.
High energy material but stable

Hypothetical Nitrogen Cage

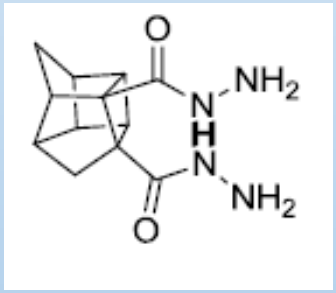
Molecules Under Study



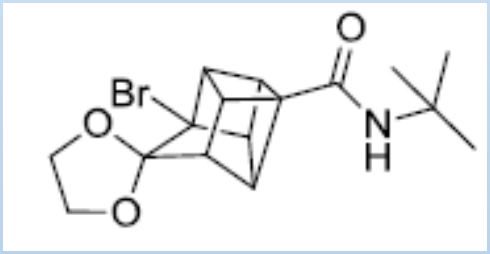
HNC1



HNC2



HNC3



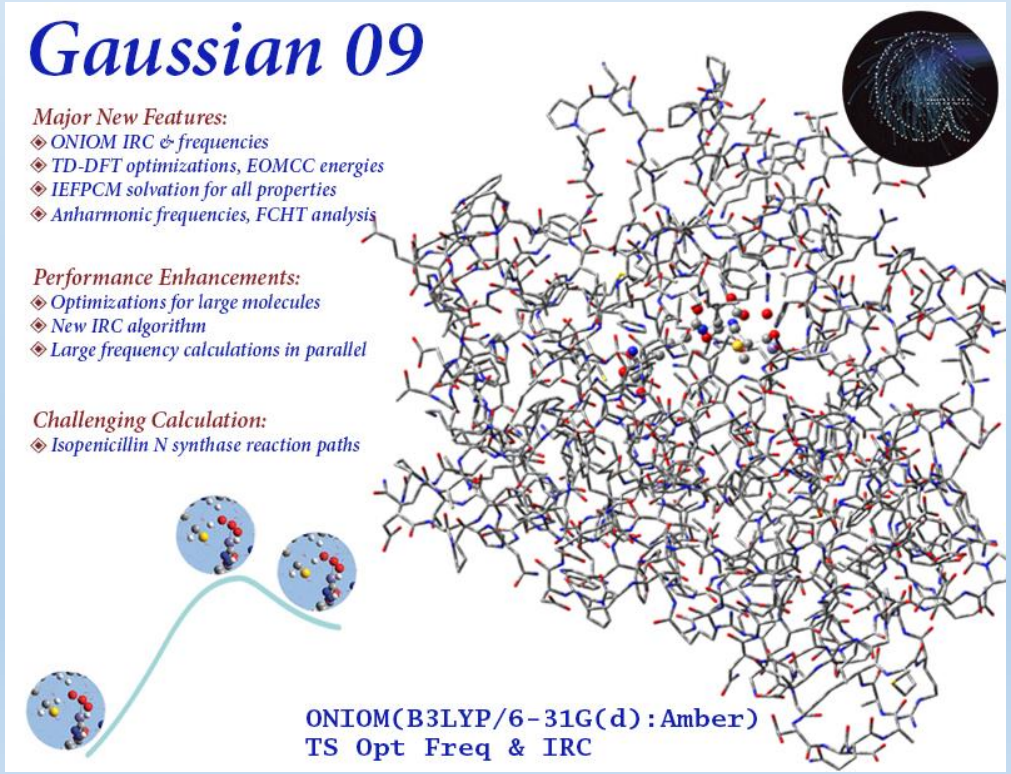
HNC4

Modifications of cubane cages with addition of nitrogen rich chains

Computational Methods - 1

There are various molecular modelling techniques in computational chemisty (Lewars, 2011).

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



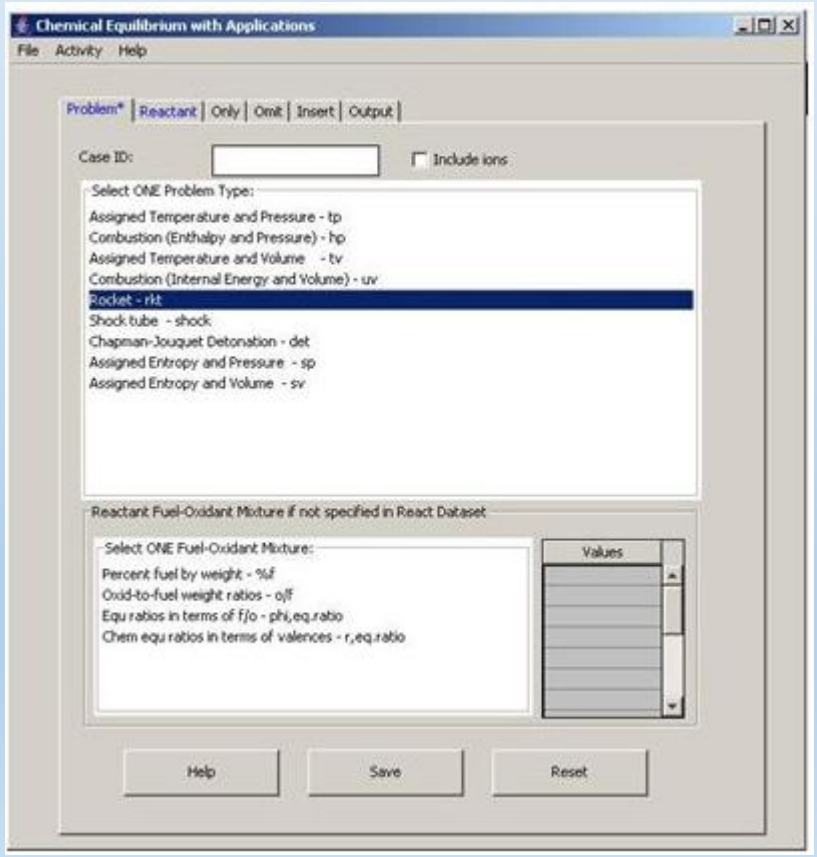
Software based on Quantum Chemistry

Computational Methods - 2

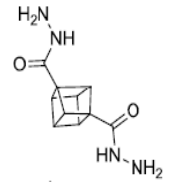
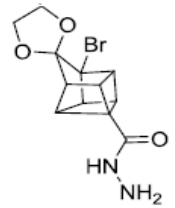
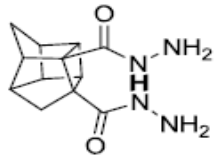
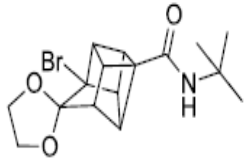
Software used for calculating propulsive properties.

NASA CEA

- *Specific Impulse (I_{sp})*
- *Density specific impulse (ρI_{sp})*
- *Adiabatic flame temperature*



Results & Discussion-1 (HNC)

Notation	Formula	Molecular structure	Heat of Formation (kcal/mol)	Density (gm/cm3)
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

Note:- HOF Cubane = 144.2 kcal/mol

Results & Discussion-2 (HNC)

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

Table 1: Performance as Solid Bipropellant with AP as oxidizer

(20% HNC, 80% AP)

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

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

Table 2: Performance as additive to AP-HTPB mixture

(80% AP, 15% HTPB, 5%HNC)

AP : Ammonium Perchlorate

HTPB : Hydroxyl terminated polybutadiene

Results & Discussion-3 (HNC)

Compound	O/F Ratio	CCT (K)	Ratio √(Tad/MW)	I_{sp} (s)	$I_{sp,vac}$(s)	ρI_{sp} (gm.s/cm^3)	$\rho I_{sp,vac}$ (gm.s/cm^3)
$C_{10}H_{12}N_4O_2$	1.14	3861.76	12.15	352.40	366.73	459.53	478.22
$C_{10}H_8N_8$	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

Table 3: Performance as propellant with LOX as oxidizer

Results & Discussion-4 (HNC)

Compound	O/F Ratio	CCT (K)	Ratio √(Tad/MW)	I_{sp} (s)	$I_{sp,vac}$ (s)	ρI_{sp} (gm.s/cm^3)	$\rho I_{sp,vac}$ (gm.s/cm^3)
$C_{10}H_{12}N_4O_2$	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

Table 4 : Performance as additive to RP-1 with LOX as oxidizer (30% HNC, 70 % RP-1)

Results & Discussion-5 (HNC)

Compound	CCT (K)	Ratio √(Tad/MW)	I_{sp} (s)	$I_{sp,vac}$(s)	ρI_{sp} (gm.s/cm^3)	$\rho I_{sp,vac}$ (gm.s/cm^3)
$C_{10}H_{12}N_4O_2$	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

Table 5: Performance as Monopropellant

Results & Discussion-6 (HNC)

Table 5: $\rho I_{sp,vac}$ from last 3 mixtures

Compound	HNC+LOX $\rho I_{sp,vac}$ (gm.s/cm^3)	HNC+RP1+LOX $\rho I_{sp,vac}$ (gm.s/cm^3)	Mono $\rho I_{sp,vac}$ (gm.s/cm^3)
$C_{10}H_{12}N_4O_2$	478.22	404.05	424.17
$C_{12}H_{13}N_2O_3Br$	432.63	441.69	396.68
$C_{12}H_{16}N_4O_2$	453.15	419.52	340.48
$C_{16}H_{20}NO_3Br$	450.33	424.85	324.71

Table 6: 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 $gm.s/cm3$

Compare the values

Results & Discussion-7 (HNC)

Compound	Detonation Pressure, D (kBar)	Detonation Velocity, V (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

Table 6: Predicted* detonation properties

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

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

where ρ (g/cm3) 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).

* Detonation properties not computed if Q is negative

HNC- Conclusion

- Results of propulsive properties under 5 different mixture combinations are presented
  1. As solid bipropellant with AP as oxidiser (80% AP, 20% HNC)
  2. As additive to AP-HTPB mixture (80% AP, 15% HTPB, 5%HNC)
  3. As propellant with LOX as oxidiser
  4. As additive to RP1 with LOX as oxidiser (30%HNC, 70% RP1)
  5. As monopropellant
- Detonation properties (Pressure and Velocity) are tabulated.

✓ Specific impulse values show that these HNC compounds are better than currently used compounds by a small factor (compare tables 5 & 6)

✓ I_{sp} values roughly follow the trend

LOX (table3) > RP1, LOX (table4) > Monopropellant(table5) > AP (table1) > HTPB, AP (table2)

✓Heavier atoms like Br tend to reduce overall effectivity sometimes, though not a sweeping conclusion

✓The detonation properties are not as good as that of RDX (DP = 35.1Gpa, DV = 8.93 m/s)[*]

[*] 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.

Topic 2

Chemical Reaction Mechanism (CRM)

PTFE (*aka* Teflon) + Aluminium Nano-particles in presence of solvents

Literature Review - CRM

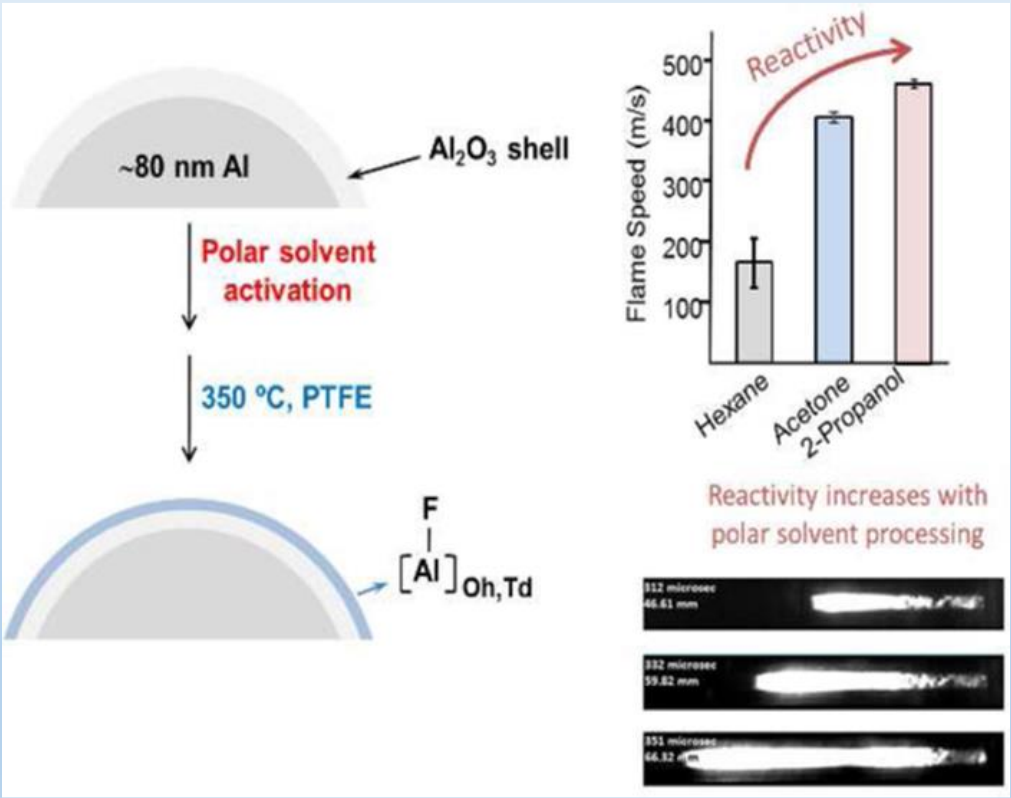
- PTFE (Polytetrafluoroethylene) and Aluminium Nano particles reaction is of interest [*]

- Solvent used in preparation reaction mixtures affects thermal properties. Flame speeds, DSC (differential scanning calorimetry) measurements.

- Possible reason : Pre ignition reaction (PIR)
  - Occurs before primary combustion at ~ 510 °C
  - Strengthened by MDM (melt dispersion mechanism)
  - Tiny Al-F layer over the 3nm thick Al_2O_3 shell.
- Polar solvents > Non polar solvents > No solvation

observed trend in [*]

Solvent effect



[*] 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

Computational Methods-1

- Gaussian software

- Calculation framework:

1. Basic reactants, products optimisation + frequency using CBSQB3 theory

2. Scan calculation to find Transition State (TS) of the reaction using simple theory

3. Transition State (TS) 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 optimisation using CBSQB3 theory, which is a high level theory

6. Find the kinetics, thermochemical parameters (activation energies, G,H, kf ,kb etc) using transition state theory mentioned earlier.

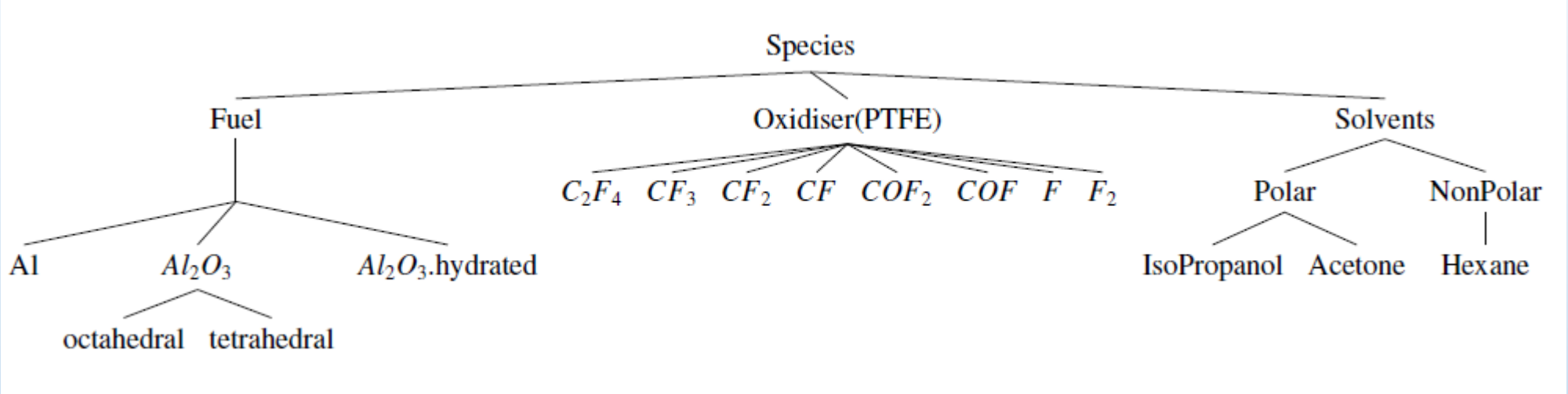
Computational Methods-2

- **Heat of formation of a compound $A_x B_y H_z$ [*]:**

$$\Delta H^0_f (A_x B_y H_z, 298\ K) = \Delta H^0_f(A_xB_yH_z, 0\ K) + [H^0(A_xB_yH_z, 298\ K) - H^0(A_xB_yH_z, 0\ K)]$$
$$- x[H^0(A, 298\ K) - H^0(A, 0\ K)]_{st}$$
$$- y[H^0(B, 298\ K) - H^0(B, 0\ K)]_{st}$$
$$- z[H^0(H, 298\ K) - H^0(H, 0\ K)]_{st}$$

[*] Lewars, E.G., *Computational chemistry: introduction to the theory and applications of molecular and quantum mechanics*. 2010: Springer Science & Business Media.

Possible pathways



Suggested reaction categories

- Al_2O_3-OH + F containing radical –> Al_2O_3-F + OH^- + Other Products
- Solvent + F containing radical –> F substituted solvent.
- Al_2O_3-OH + F substituted solvent –> Al_2O_3-F + Solvent
- Solvent –> Decomposition products

CRM - Conclusion

- Proposed methodology has been verified by trying it out for the reaction

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

- Possible reactions pathways have been identified for interaction between Alumina and PTFE decomposition products.

Future Work

- HNC compound analysis is complete. All the results are available now.

- All the reactions from part 2 will be simulated in the next semester. CRM formulation will be finished in BTP 2.

References

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


To Infinity and Beyond !
Thank you
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