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Group tuesday 18:15-20:00
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MKWS project

Analysis of composition and temperature of products of hydrazine thermal decomposition

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Contents

1 Introduction

Purpose of the project was to analyse composition and temperature od products of hydrazine thermal decomposition. Analysis was performed with code written in Python programming language. Code makes extensive use of Cantera library to simulate changes in thermodynamic state of system during hydrazine decomposition.

2 Theoretical background

2.1 Hydrazine description

Hydrazine is a chemical compound with a chemical formula N_2H_4. In atmospheric conditions hydrazine is a fuming liquid. It is highly toxic to humans and highly flammable. Its most common use is as a propellant in rocket science, either in hypergolic combustion with nitrogen tetroxide (as in a RCS system of a space shuttle [1]), or as a mono-propellant.

2.2 Hydrazine decomposition

Decomposition is a type of chemical reaction where a substrate breaks into simpler compounds. Thermal decomposition is a type of decomposition in which breakdown is caused by heating of substrates. Decomposition of hydrazine may be written in short as
$3\,N_2H_4 \longrightarrow 4\,(1-x)NH_3 + (1+2\,x)N_2 + 6\,xH_2$ [2]. Complete set of equations governing kinetics of thermal decomposition of hydrazine in atmospheric pressure and temperature of 1000 K has been described in [3].

3 Model description

Model of hydrazine decomposition presented in [3] includes 51 chemical reactions, 5 compounds (H_2 [hydrogen], N_2 [nitrogen], NH_3 [ammonia], N_2H_2 [diazene] and N_2H_4 [hydrazine]) and 6 radicals (H, N, NH, NH_2, NNH and N_2H_3). Since no Cantera input file describing those reactions was found, a custom input file was developed. Characteristics of H, H_2, N, N_2, NH, NH_2, NH_3 and NNH were taken from gri30.yaml official Cantera input file. Characteristics of N_2H_2, N_2H_3 and N_2H_4 were taken from [4]. Reactions and their coefficients for Arrhenius equation were taken from [3]. Such prepared input file was named N2H4.yaml and is attached under directory MKWS/ct-env/share/cantera/data/N2H4.yaml.

Next, a code for analysis of decomposition of hydrazine was developed. First, the initial conditions of 1000 K, 101325 Pa and 100% concentration of hydrazine were set for mixture. Then analysis was performed in three steps. In first step thermodynamic equilibrium of the mixture was found with use of equilibrate function. Method of constant pressure and enthalpy was used. Then 2 microseconds of an evolution of a constant pressure reactor filled with prepared mixture was simulated by placing ConstPressureReactor object in ReactorNet object. This resulted in graphs of changes of temperature, hydrazine, hydrogen, nitrogen and ammonia concentrations in time. Finally, results from the reactor simulation were compared with results of thermodynamic equilibrium to check whether simulation time should be increased.

Model of constant pressure and enthalpy was used because it is the best approximation of combustion chamber of rocket thruster in stable conditions.

4 Results

As a result composition and temperature of products has been acquired, as well as graphs of changes in temperature and in concentration of certain compounds. In table 1 comparison between pre-reaction mixture, mixture in thermodynamic equilibrium and mixture obtained as a result of simulation is made. Presented are values of temperature in units of Kelvin and molar concentrations of certain compounds in percent. Complete data on pre-reacted mixture may be found in attached file "substratesOrg". Complete data on mixture in thermodynamic equilibrium may be found in attached file "productsOrg". Complete data on mixture resulting from a simulation may be found in attached file "productsReactorOrg".

Parameter	Initial mixture	Termodynamic equilibrium (by .equilibrate method)	Simulation result (by .ReactorNet method)
T [K]	1000	1883.7	1883.8
H_2 [%]	0	0.666	0.666
N_2 [%]	0	0.333	0.333
NH_3 [%]	0	$\sim$0	$\sim$0
N_2H_4 [%]	1	$\sim$0	$\sim$0

Table 1: Comparison of molar concentration and mixture temperatures before and after decomposition

Changes in temperature of the mixture was presented on graph 1. Changes in molar concentration are shown on graphs: N_2H_4 on graph 2, H_2 on graph 3, N_2 on graph 4 and NH_3 on graph 5.

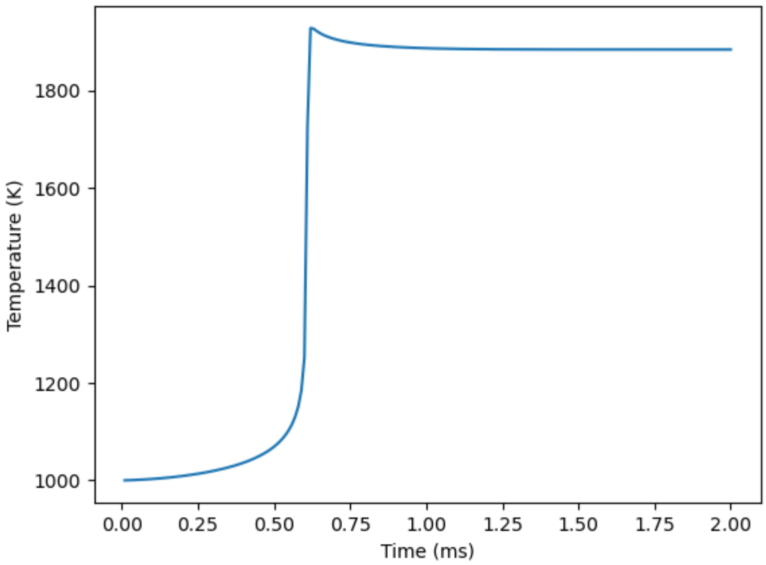

Figure 1: Changes in temperature of the mixture

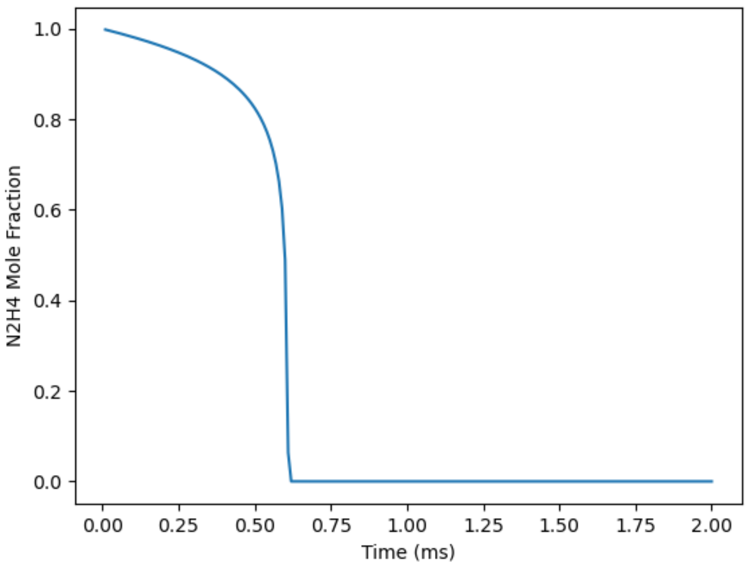

Figure 2: Changes in molar concentration of hydrazine

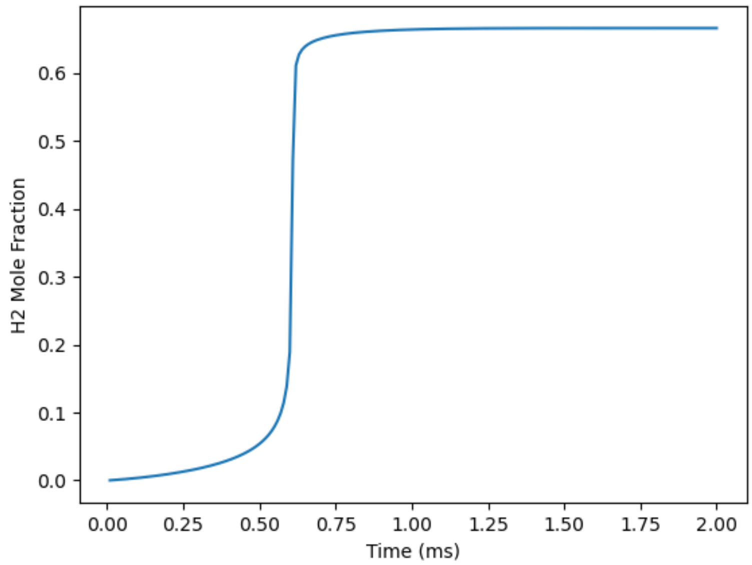

Figure 3: Changes in molar concentration of hydrogen

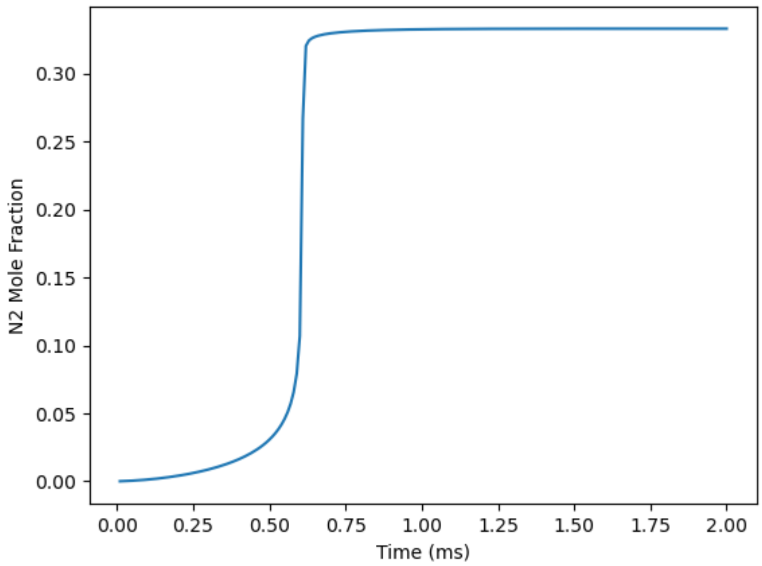

Figure 4: Changes in molar concentration of nitrogen

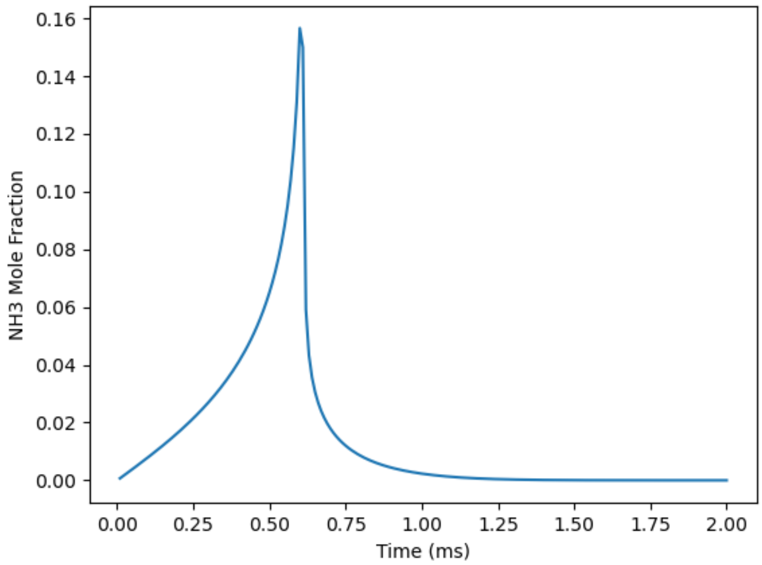

Figure 5: Changes in molar concentration of ammonia

5 Discussion of the results

There is little to no discrepancy between state of the mixture in thermodynamic equilibrium and simulation results. During thermal decomposition of hydrazine in constant enthalpy and pressure model temperature of mixture rises, therefore such reaction is exothermic. Temperature rises as concentration of hydrazine falls, reaching maximum value of 1928 K in the moment when supply of hydrazine is depleted. Ammonia concentration also reaches its maximum of 15,8% in the moment when supply of hydrazine is depleted. After depletion of hydrazine endothermic decomposition of ammonia becomes dominant and causes temperature of the mixture to drop a by few Kelvins. Then at the temperature of 1883 K creation-destruction reactions of ammonia reach equilibrium and keep concentration of ammonia near 0%. The only compounds found in products in large quantities are hydrogen and nitrogen, with exact values presented in table 1.

In section 2.2 an overall equation of hydrazine decomposition was shown. Best fit to simulation results yields substituting x=1.1 to this equation. This however would result in negative amount of ammonia in reaction products, which is clearly an error. This result is quite possibly due to exclusion of other products of decomposition (including radicals) from this equation. Concentrations of those other products may be found in files "productsOrg" and "productsReactorOrg" attached to this report.

It is very possible that maximal temperature of the mixture would me higher if ammonia was removed from the reactor without giving it time to decompose. If this assumption is true it would be an important consideration while designing hydrazine rocket thrusters, since temperature inside combustion chamber is one of the most important factors while calculating specific impulse. By removing ammonia from the chamber at the right rate temperature inside chamber could be risen without changing fuel consumption.

6 Summary

A simulation of decomposition of hydrazine was performed. Results are within reasonable bounds. Python programming language with Cantera library provide easy to use and effective way to analyse complex thermodynamic problems i gases. Only a few out of many functionalities of Cantera were used in this project.

References

[1] Blevins, D.R., Hohmann, C.W., DESCRIPTION OF THE SPACE SHUTTLE REACTION CONTROL SYSTEM, AIAA PAPER NO. 75-1299 `https://ntrs.nasa.gov/citations/19750061613`

[2] HAROLD W. LUCIEN, Thermal Decomposition of Hydrazine, JOURNAL OF CHEMICAL AND ENGINEERING DATA, VOL. 6, NO. 4, OCTOBER 1961, Pages 584-586

[3] A.A Konnov, J De Ruyck, Kinetic modeling of the decomposition and flames of hydrazine, Combustion and Flame, Volume 124, Issues 1–2, 2001, Pages 106-126, ISSN 0010-2180, `https://doi.org/10.1016/S0010-2180(00)00187-5`

[4] `https://raw.githubusercontent.com/Cantera/cantera-jupyter/main/data/SiF4_NH3_mec.yaml`, accessed on 06.06.2024