

Equilibrium for combustion of rocket propellant

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Mathematical Models of Technology

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Overview

- 1 Statement of the problem
- 2 Preliminary concepts
 - Review of Kinetic Molecular Theory
 - Review of Thermodynamics
- 3 Our approach to the problem

Motivation

- Rocket propellant is a material used by a rocket that reacts chemically, ejecting a reaction mass with very high speed to produce thrust, and thus provide spacecraft propulsion.
- The type of propellant varies depending on the type of rocket.
- We focus on rockets that are propelled by means of combustion reactions, which are exothermic and which happen at high temperatures.
- Under these conditions, the components dissociate, which makes the parameters of the reaction difficult to find.
- Our aim is to determine the parameters of the reaction at the same time as we provide a full open-source solver for combustion problems involving a gas mixture with dissociation.

Basics I

Conservation of Mass Law

In any chemical reaction, the sum of the masses of the reagents is equal to the sum of the masses of the products.

Ideal Gases Law

Given the pressure P , volume V and temperature T of an ideal gas,

$$PV = nRT, \quad R = 0,082 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

where n is the number of moles contained in the gas.

Basics II

Dalton's Law of Partial Pressures

The total pressure of a mixture of gases equals the sum of the partial pressures. Mathematically, given a mixture of n gases in a container,

$$P = \sum_{i=1}^n P_i, \quad P_i = n_i \frac{RT}{V} = n_i \frac{P}{n} = \frac{n_i}{n} P = \chi_i P.$$

Molar fraction

The molar fraction χ_i of the gas i is

$$\chi_i = \frac{n_i}{n} = \frac{P_i}{P} = \frac{V_i}{V}.$$

First Law of Thermodynamics

The total energy of an isolated system is constant. Mathematically, we write

$$\Delta U = Q + W,$$

where U is the internal energy, Q is the heat involved in the process and

$$W = -P_{\text{ext}}\Delta V = -\Delta nRT$$

is the work performed through compression or expansion of the system, where P_{ext} is the pressure that the exterior exerts upon the gas and Δn is the variation in the number of moles.

Constant-volume and constant-pressure reactions

Enthalpy

Let us define the *enthalpy* H as

$$H = U + PV.$$

It is important to notice that enthalpy is a thermodynamic potential, so in order to measure the enthalpy of a system, we must refer to a defined reference point. Therefore what we measure is the change in enthalpy, ΔH .

Particular cases of enthalpies

- Standard enthalpy of reaction ΔH_r^0
- Standard enthalpy of formation ΔH_f^0 for 1 mol of a substance from the basic elements in the standard states of reference
- Reticular energy
- Bond dissociation energy

One may calculate

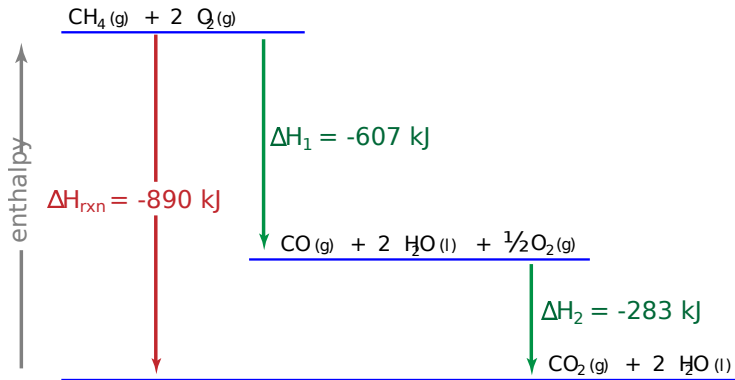
$$\Delta H_r^0 = \sum_{p \in P} \nu_p \Delta H_f^0(p) - \sum_{r \in R} \nu_r \Delta H_f^0(r),$$

where P and R are the set of products and reagents, respectively, and ν_p and ν_r are the stoichiometric coefficients in the reaction.

Enthalpy diagrams

Hess's Law

If a reaction can be expressed as the sum of several elementary reactions, then the variation in the enthalpy of the reaction can be calculated adding up the variations in the enthalpy of each elementary reaction.



Second and Third Laws of Thermodynamics

Second Law of Thermodynamics

Given a thermodynamical system, the change in entropy can be expressed as

$$\Delta S = \frac{Q_{\text{rev}}}{T},$$

where Q_{rev} is the heat that intervenes in a reversible process. Alternatively,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}} > 0.$$

Third Law of Thermodynamics

The entropy of a perfect pure crystal at 0 K is zero.

Spontaneity

If we assume that the variation in the entropy of the environment is due to $-\Delta H_{\text{system}}$ and take into account the Second Law of Thermodynamics, we get $\Delta H_{\text{system}} - T\Delta S < 0$.

Gibbs free energy

We can then conveniently define

$$G = H - TS.$$

Criteria for predicting the nature of a thermodynamic process

ΔH	ΔS	ΔG	Nature of the process
—	—	?	spontaneous for small T
—	+	—	spontaneous
+	+	?	spontaneous for large T
+	—	+	non spontaneous

Sketch of the procedure

- Chemical equilibrium is a state in which the species involved remain constant along time.
- We aim to determine some properties about a chemical reaction given the reagents. In particular, we wish to determine whether the chemical equilibrium is attained in reactions of combustion.
- There are infinitely many solutions and each one has an associated value for G .
- We can formulate a minimisation convex problem for the Gibbs free energy.
- The reaction that actually takes place is the one that has the minimum Gibbs free energy.

What has been done so far

- Creation of a whole package in a Matlab environment. This one includes:
 - the HGS function that calculates properties of mixtures of gases
 - the `fminineq` function that minimises the Gibbs free energy of a mixture of gases
- In comparison to the Matlab's `fmincon` function, `fminineq` performs successfully in a variety of cases. However, it does not even provide similar results in others.

What we intend to do

- State an optimization problem for the Gibbs? energy.
- Come up with a open-source (Python-based) numeric solving procedure for the problem.
- Compare it to the existing MATLAB (HGS Chemical Equation Solver) solution.
- Propose and explore improvements (speed, complexity, easy to use)
- Document the solution and upload it into a public repository.

What we have done so far

- State an optimization problem for the Gibbs? energy.
- Get familiar with the existing Matlab software (Burcat chemical elements database as well as the functions `fmincon`, `fminineq` and `hgs`).
- Start to programme a python-based solver.

Thanks for your attention!!

