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Internal Flow of a Rocket Engine Nozzle Calculated Through One-Dimensional Equilibrium

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ABSTRACT

Modeling of the internal flow of a nozzle is a vital step in the design of a rocket engine. This study focuses on providing an in-depth examination of a thermochemical rocket engine's operation through chemical equilibrium. The computation extends to cover both gaseous and condensed species, as well as phase transitions, offering a comprehensive understanding of the engine's behavior. Notably, this research introduces the ability to freeze the composition at any chosen point within the nozzle, allowing for tailored modeling to specific engine conditions and enhancing its versatility as a tool for analysis and design. Moreover, the study takes an additional step by calculating the transport properties along the nozzle. Special note is made of the difference between equilibrium and frozen variables. By integrating equilibrium composition, condensed species, and transport properties, this research exemplifies a holistic approach to analyzing and optimizing the performance of thermochemical rocket engines, with several illustrative examples showcasing the capabilities of the program.

Keywords: Chemical equilibrium; Rocket engine design; Internal flow; Rocket nozzles; Transport properties.

INTRODUCTION

Rocket engines, crucial for space exploration and aerospace advancement, rely on chemical reactions to generate thrust. These reactions occur under extreme conditions of temperature and pressure, as well as carefully selected fuel-to-oxidizer ratios. To understand and optimize these engines, it is common to use equilibrium composition calculations, as the residence time of the gases within the chamber is typically much longer than the characteristic chemical reaction times. In the context of rocket propulsion, the utilization of equilibrium composition calculations within the combustion chamber, followed by dynamic equilibrium calculations in the nozzle, stems from the inherent differences in flow conditions and timescales encountered within these two regions of the engine.

As the hot gases exit the combustion chamber and enter the nozzle, they experience a gradual drop in pressure and temperature. In spite of this, for many engines, the residence time in the nozzle is still relatively long compared to the chemical reaction time. Therefore, equilibrium calculations continue to be applicable as the composition adjusts to the new thermodynamic conditions. However, as the gases continue to expand in the nozzle, there comes a point where the changes in temperature and pressure happen so rapidly that chemical reaction rates are unable to keep up. The temperature drops significantly, causing the reactions to

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essentially "freeze" or become negligible. At this stage, the assumption of "frozen flow" is adopted for simplification, as chemical reactions are considered nearly stopped in the simulation model.

Since equilibrium composition calculations are essential blueprints for rocket engine design, they need to be performed from a very early design stage. They provide a scientific foundation to comprehend how variations in parameters such as temperature, pressure, and fuel-oxidizer ratio affect the composition of combustion products. Consequently, the use of complex CFD tools is not a viable option due to their long setup and computation times. Therefore, software such as the one developed, capable of simulating the internal flow of the engine in less than a second, proves to be a great advantage.

At the beginning of the 1950s, the calculation approaches were based on the method of equilibrium constants that Brinkley (1947) adapted for the computation of systems with a high number of components. The method is direct and intuitive and was improved over the years by making it more robust, as, for example, shown in Villars (1959). Other improvements focused on calculation speed, such as the one presented by Smith and Missen (1968). At this point in time, the first works in the NACA Lewis FPL were published. This included pioneering work in the calculation of equilibrium composition by Morrell (1951). Furthermore, useful databases were established for the thermophysical properties of the components by Huff and Gordon (1950), all collected in the NACA Report 1037 by Huff *et al.* (1951). Further advancements throughout the decade include the improvement of the calculation process by Zeleznik and Gordon (1960), tabulation of thermodynamic data by Zeleznik and Gordon (1962a; b), and the incorporation of the equilibrium composition model into calculation processes of aeronautical interest, such as Zeleznik and Gordon (1962a; b). There were also additional efforts made by other agents and institutions, such as Rocketdyne (a division created by North American Aviation in those years), where new formulations of solid propellant were developed by Morgan *et al.* (1956). The development used novel methods to determine the specific impulse, which did not always consist of strict calculations of the equilibrium composition.

In this work, a new freely accessible software (ODEKO) was developed. It is capable of simulating the internal flow of chemical rocket engines through chemical equilibrium and/or frozen flow. Compared to existing software, it adds the capability to switch between "equilibrium" and "frozen" computation at any point of the nozzle. Moreover, it gives the thermodynamic and transport properties for all points of the nozzle, allowing the user to choose whether "frozen" or "equilibrium" variables should be displayed.

Firstly, a summary of other existing software for the simulation of chemical equilibrium will be presented. Subsequently, the theory behind equilibrium calculations will be explained in the next section, with emphasis on the computation of phase changes. Afterwards, the difference between "frozen" and "equilibrium" thermodynamic and transport properties will be shown along with the equations required for their computation. The specifics of the application for rocket engines will be highlighted next. Lastly, results obtained with the developed software will be presented, to exemplify the effects of equilibrium or frozen simulations. The conclusion to this work is given in the last section.

Revision of equilibrium composition codes

In the mid-20th century, in the early days of rocket engine development, interest sparked in the creation of reliable and accurate procedures to calculate the propulsive characteristics of thermochemical rocket engines. The first difficulties were noticed early on. The first challenge was to develop flexible and general calculation procedures that would allow the inclusion of an arbitrary number of species. An additional challenge, and no less important, was to have thermophysical data of the species in the range of temperatures of interest. The best-known effort in this regard is that of the researchers of the National Aeronautics and Space Administration (NASA) Glenn Research Center (which in those years was called the National Advisory Committee for Aeronautics [NACA] Lewis Flight Propulsion Laboratory), who for 30 years developed one of the best-known and longest-lived computer codes of aerospace engineering. Currently, the program is called Chemical Equilibrium with Applications (CEA), and the latest updates are from Gordon and McBride (1994) and from McBride and Gordon (1996).

At the same time, in the late 1950s, the Naval Weapons Center at China Lake began the development of an equilibrium composition calculation code (Browne *et al.* 1960; Cruise 1964; 1979). The program was initially called Propellant Evaluation Program (PEP), and numerous revisions such as Brown (1995), Dobbs and Grubelich (2001), and adaptations that reach our days (Cooper 2016) have been derived in various forms useful for research and amateur rocketry. The equilibrium constants method consists of a variable number of equations and generates a nonlinear system, which is difficult to handle. The difficulties of providing

an initial solution, the need for convergence acceleration methods, and the inclusion of condensed species present a number of complications that were detrimental to the robustness and reliability of the calculations. In White *et al.* (1958), it is proposed to use the Gibbs free energy minimization method to compute the equilibrium composition. This approach is very successful as it is not necessary to have an explicit list of chemical reactions, sufficing with a list of substances. Additionally, the problems of interest are generally dealt with successfully, even with condensed species. For this reason, most initiatives since then use this method and only some older codes, or codes derived from them, retain formulations based on equilibrium constants. Typically, these latter programs address very specific problems of internal ballistics of gun propellants. The computer code that gave rise to NASA Glenn's CEA was rewritten to use the Gibbs' free energy minimization method to compute equilibrium composition, based on the developments of White *et al.* (1958), whose results were described by Zeleznik and Gordon (1960).

The development of the CEA code spans 30 years. At the end of the 1950s, the first codes were written, which used the calculation of equilibrium composition to obtain the propulsive properties of a rocket (Gordon *et al.* 1959). This program was improved during the 1960s in Gordon and Zeleznik (1962; 1963) and Zeleznik and Gordon (1962a; 1968), enhancing polynomial adjustments of thermodynamic properties, adding practical applications, making comparative studies on resolution methods, and including the case of Chapman-Jouguet detonations. This code used a modified version of the iteration procedure for chemical equilibrium that required no special initial estimates for composition, constraints on mass balance, or equilibrium ratios during iterations, as described in Huff *et al.* (1951). This was the first widely distributed version of the Lewis chemical equilibrium code (CEC). As the reliability and accuracy of the results obtained with the code depended in depth on the thermodynamic data used, much work was always invested in improving and updating the thermophysical data of the substances used (McBride *et al.* 1963; McBride and Gordon 1961).

Subsequently, McBride and Gordon (1967) consolidated and documented the computer codes used to calculate and fit thermodynamic data into a single code, called PAC1. During the 1960s, the rewriting of the equilibrium composition calculation program was tackled. The resulting code was called CEC (Gordon and McBride 1976) and was widely distributed. The iterative equations used to obtain equilibrium compositions were derived from the minimization of the Gibbs function. This version did not yet include the calculation of transport and finite area properties. The next version of the code was called CET (McBride *et al.* 1993) and was widely distributed, constituting one of the most cited versions. Nevertheless, the current version, and the one used nowadays, is called CEA (Gordon and McBride 1994; McBride and Gordon 1996). The employed methodology has proved to be very robust and fruitful, and it has been used in the creation of numerous applications for the analysis of thermochemical engines, as in Filipović and Kilibarda (2000; 2001). For the analysis of solid propellant rocket engines, Terzic *et al.* (2010) propose a set of applications that compute equilibrium composition by minimizing Gibbs free energy.

There are a number of programs with diverse capabilities that provide the equilibrium composition of reactive mixtures. Often, such programs are oriented toward the internal ballistics of propellants and explosives, requiring them to give reliable data at high pressures and temperatures. The REAL program, written by Belov (1998), obtains the composition under the condition of maximum entropy and can work with several equations of state that take into account real effects due to high pressures. Another example is the KHT code, written by Tanaka (1986), whose use is specifically oriented to the analysis of detonations. Based on the work of NASA Lewis, with the method of mass action, the ICT program was developed by Terzic *et al.* (2010), using the minimization of Gibbs free energy. It ended up becoming a general-purpose program (Noläng 1983) called EKVI-System. Another code with similar functions is BLAKE (Freedman 1973; 1982; 1998), which allows the use of virial equations and is based on TIGER (Wieberson *et al.* 1968). Further examples include the program CERV (Wong *et al.* 2004), which deals with complex mixtures, minimizing the Gibbs energy but using reaction variables. The TIGER code was originally developed at the Stanford Research Institute by Wieberson *et al.* (1968), for the calculation of equilibrium composition with heterogeneous mixtures and arbitrary equations of state, based on the theoretical development by Brinkley (1947). Further developments of the program can be found in Cowperthwaite and Zwisler (1974; 1982). As TIGER initially allowed the use of any equation of state, it facilitated the writing of BLAKE using a modified virial equation, meant to be used in internal ballistics calculations of military propellants. In principle, TIGER is a program meant for the calculation of composition and properties of detonations. On the other hand, BLAKE specializes in calculations of internal ballistics in gun propellants. The CERV code was developed to determine complex

equilibrium compositions of non-ideal mixtures of numerous imperfect gases, as well as, compressible liquid and solid species with phase transitions, for closed-vessel applications. This code minimizes Gibbs energy using reaction variables, in contrast to others. Several of the aforementioned codes are tested in detail in Koch *et al.* (2009). The Bac and Bagheera (1984) code was developed in the 1980s and 1990s in France for similar purposes. It is based on an ideal mixture model, a modified virial equation of state and includes the volumes of condensed species. By the early 1990s, the Bagheera code supplanted the BLAKE code as the standard for military applications in NATO countries.

Equilibrium calculations

The condition for chemical equilibrium is the minimization of free energy. In this case, Gibbs energy will be minimized (note that the minimization of Helmholtz energy may also be used, although it is not meant for constant pressure problems, characteristic of a rocket engine).

As seen in Gordon and McBride (1994), the iteration equations become:

$$\Delta \ln n_j = \sum_{i=1}^{NE} a_{ij}\pi_i + \Delta \ln n + \frac{H_j^o}{RT}\Delta \ln T - \frac{\xi_j}{RT} \qquad (j = 1, ..., NG) \tag{1}$$

$$-\sum_{i=1}^{NE} a_{ij}\pi_i - \frac{H_j^o}{RT}\Delta \ln T = -\frac{\xi}{RT} \qquad (j = NG+1, ..., NS) \tag{2}$$

$$\sum_{j=1}^{NG} a_{ij} n_j \Delta \ln n_j + \sum_{j=NG+1}^{NS} a_{ij}\Delta n_j = b_i^o - b_i \qquad (i = 1, ..., NE) \tag{3}$$

$$\sum_{j=1}^{NG} n_j \Delta \ln n_j - n\Delta \ln n = n - \sum_{j=1}^{NG} n_j \tag{4}$$

$$\sum_{j=1}^{NG} \frac{n_j H_j^o}{RT}\Delta \ln n_j + \sum_{j=NG+1}^{NS} \frac{H_j^o}{RT}\Delta n_j + \left(\sum_{j=1}^{NS} \frac{n_j C_{p,j}^o}{R}\right)\Delta \ln T = \frac{h_0 - h}{RT} \tag{5}$$

$$\sum_{j=1}^{NG} \frac{n_j S_j}{R}\Delta n_j + \sum_{j=NG+1}^{NS} \frac{S_j^o}{R}\Delta n_j + \left(\sum_{j=1}^{NS} \frac{n_j C_{p,j}^o}{R}\right)\Delta \ln T = \frac{s_0 - s}{R} + n - \sum_{j=1}^{NG} n_j \tag{6}$$

Where $\pi_i = -\lambda_i/RT$ and n_j represents the kg-mol of specie j per kg of mixture. The term b_i represents the kg-atoms of an element per kg of mixture (of propellant in the case of b^o) and a_{ij} represent the kg-atoms of element i per kg-mol of specie j.

For chemical equilibrium in the combustion chamber, enthalpy remains constant (since a combustion is taking place); therefore, Eqs. 1–5 are used. Throughout the nozzle entropy is conserved, resulting in Eqs. 1–4 and 6 being used. The conservation of entropy in the nozzle is a result of considering it adiabatic (no heat flow), disregarding viscosity and reaction terms canceling out due to the chemical equilibrium condition. This last fact can be proven (as seen in Tizón Pulido and Jenaro de Mencos [2018]) by writing the entropy differential:

$$TdS = d\left[\sum_{j=1}^{NS} n_j H_j^o\right] - \frac{1}{\rho}dP - \sum_{j=1}^{NS} \xi_j dn_j \tag{7}$$

If the equations of energy and momentum are substituted into Eq. 7, the following expression is obtained:

$$TdS = -\sum_{j=1}^{NS} \xi_j dn_j = -dg \tag{8}$$

Which is identically zero, since the equilibrium criterion is the minimization of Gibbs free energy ($dg = 0$).

Convergence criteria

The value for a new iteration (k+1) is obtained in the following manner:

$$\begin{aligned} \ln n_j{}^{(k+1)} &= \ln n_j{}^{(k)} + \varepsilon^{(k)} (\Delta \ln n_j)^{(k)} \qquad (j = 1, ..., NG) \\ n_j^{(k+1)} &= n_j^{(k)} + \varepsilon^{(k)} (\Delta n_j)^{(k)} \qquad (j = NG+1, ..., NS) \\ \ln n^{(k+1)} &= \ln (k) + \varepsilon^{(k)} (\Delta \ln n)^{(k)} \\ \ln T^{(k+1)} &= \ln T^{(k)} + \varepsilon^{(k)} (\Delta \ln T)^{(k)} \end{aligned} \tag{9}$$

The values used in the first iteration are preset estimates, which can be changed in the preferences menu of the software at any time. If the value of n for a given specie drops below a certain threshold, it is automatically set to 0. The value for $\varepsilon^{(k)}$ is a correction factor, meant to avoid drastic changes in values, which may affect convergence capabilities. Said factor is typically computed as presented in Gordon and McBride (1994).

The convergence criteria are written in Eq. 10. Note that the values written for convergence represent the default values chosen in Gordon and McBride (1994) but they can be changed to other reasonable values in the preferences menu of ODEKO, the developed software:

$$\begin{aligned} \frac{n_j |\Delta \ln n_j|}{\sum_{j=1}^{NS} n_j} &\leq 0.5 \cdot 10^{-5} \qquad (j = 1, ..., NG) \\ \frac{|\Delta n_j|}{\sum_{j=1}^{NS}} &\leq 0.5 \cdot 10^{-5} \qquad (j = NG+1, ..., NS) \\ \left| b_i^0 - b_i \right| &\leq (b_i^0)_m ax \cdot 10^{-6} \qquad (i = 1, ..., NE) \\ |\Delta \ln T| &\leq 10^{-4} \left| \frac{s_0 - s}{R} \right| \leq 0.5 \cdot 10^{-4} \end{aligned} \tag{10}$$

Ions

If ions are present in the mixture, several details must be kept in mind. Firstly, if all ions were to disappear from the iteration (drop below the minimum value and their n be set to 0), the equilibrium equation for electrons would not be well defined. In this case, said equation must be removed. Moreover, the presence of ions in the mixture requires an additional convergence test, as shown in Gordon and McBride (1994):

$$|\Delta \pi_e| = \left| \frac{-\sum_{j=1}^{NG} a_{ej} n_j}{\sum_{j=1}^{NG} a_{ej}^2 n_j} \right| \leq 0.0001 \tag{11}$$

If the test is not passed, the values of the ionic species must be altered as indicated by Eq. 12 until the test is successfully passed:

$$(\ln n_j)^{(k+1)} = (\ln n_j)^{(k)} + a_{ej}\Delta\pi_e \qquad (j = 1, ..., NG) \tag{12}$$

Note that, if only positive or only negative ions are present, the ion balance can never be achieved, and, therefore, ions must be removed from the mixture. Additionally, in the case where a new equilibrium is calculated using a previous one as a seed for the iterations, the ion equation should be introduced even if ions were previously removed, because ions might be present in the new mixture. This corresponds to the approach taken by Gordon and McBride (1994).

Condensed phases

Initially, only gaseous species and ions are considered in the mix. After convergence, a test is performed in order to check if any condensed phases should be added:

$$\frac{\delta G}{\delta n_j} = \left(\frac{\xi_j^o}{RT}\right)_c - \sum_{i=1}^{NE} \pi_i a_{ij} < 0 \tag{13}$$

If more than one condensed species passes the test in Eq. 13, the one that decreases Gibbs energy the most (has the most negative value in Eq. 13) is added. In Gordon and McBride (1994), it is recommended to divide the quantity computed in 13 by the molecular mass. This leads to better results whenever more than one species passes the test and their values have to be compared.

Once the program converges again, the test is re-conducted. This process continues until no more condensed phases are added or removed. After every convergence, if the value of n_j for a condensed species is negative, it is removed from the mixture.

Furthermore, only species that can exist at the temperature achieved after convergence are checked. After every convergence, it is also checked if any condensed species are no longer in their valid temperature range, which results in them being removed from the mixture. Note that only one species can be removed due to this condition; afterwards, a new equilibrium will be reached, and the condition in Eq. 13 will be re-checked. If no condensed species pass the test, the temperature range condition will also be re-checked. This process is continued until no more species are added or removed.

Whenever a condensed species with $n_j \neq 0$ is removed, it is recommended to reset all mixture components, since it is possible that said condensed species was the only one to have a specific atom in its composition. Therefore, after its removal, it may be difficult for the program to reintroduce said atom into the mixture, requiring lots of iterations or even failing to achieve it. Nonetheless, if a specific atom is unintentionally removed from the mixture, soft resets are set in place in the program in order to reintroduce it.

Alternative methods for condensed phases are present in the literature. The advantage of the presented method is that it does not require the user, nor the program, to establish a relation between condensed phases and gas phases, focusing exclusively on the minimization of Gibbs free energy. It is important to note that this method generally requires many iterations, since the primary equations need to converge multiple times in order to check for possible condensed phases.

Gas constant for the mixture

If condensed phases are present, the perfect gas equation can only be applied to the gaseous subset. Nevertheless, it is useful to define a new gas constant in order to include the effects of the presence of condensed species. Therefore, the gas constant used when condensed phases are present is:

$$R_g^{'} = R\left(\sum_{j=1}^{NG} n_j\right)\left(1 - \sum_{j=NG+1}^{NS} \mathcal{M}_j n_j\right) \tag{14}$$

In order for this new gas constant to be valid, the flow must be strongly interacting with the condensed phase, meaning that their temperatures and velocities must match at all times, which is explained in detail in Tizón Pulido and Jenaro de Mencos (2018).

Phase changes between condensed phases throughout the nozzle

If a condensed phase (generally a liquid) is present in the combustion chamber or throughout the nozzle, a phase change between condensed species might arise. Since the temperature is decreasing along the nozzle, it may reach the value at which the liquid phase transitions to its solid state. Said transition cannot be modelled as instant in time nor space. Therefore, during a given nozzle region, both species coexist. In this region in which the phase change takes place, the flow is isothermal as well as isentropic.

Once the phase transition temperature is reached, it is maintained constant until the original specie has completely disappeared. At the phase transition, the chemical potentials for both condensed species coincide (the least-squares coefficients are fitted to ensure this fact). As will be seen in the presented results, a notable discontinuity will be present for many variables, the most critical being the speed of sound.

The system of equations does not need to be modified and can be solved normally. Nonetheless, it is important to make sure that both species are allowed to coexist in the code. This is easily achieved by slightly increasing the temperature range in which they are defined, for an overlap to be present. Moreover, it is convenient to include a check to test if the phase transition is taking place, as some changes will need to be applied to compute the equilibrium variables (as shown in the results section).

Frozen and equilibrium thermodynamic properties

Throughout this section, values for "frozen" and "equilibrium" properties are calculated. Typically, only frozen values are used; however, as will be seen later, at times it is required to use the "equilibrium" values. This is especially so when applying equations that are usually meant for non-reacting flows (such as the M = 1 condition at the throat of the nozzle). The "equilibrium" values do not necessarily carry a physical meaning, in contrast to their "frozen" counterparts. Nonetheless, they introduce the effect of chemical equilibrium into formulas that will be used in the following sections.

The thermodynamic relations between C_p, C_v, γ, a are different for the equilibrium variables (Eq. 16), when compared to the usual "frozen variable" expressions (Eq. 15). The required computations to obtain the equilibrium variables (mainly the calculation of the derivatives present in the expressions) is detailed in Gordon and McBride (1994):

$$\begin{aligned} C_{v,f} &= C_{p,f} - R_g \\ \gamma &= \frac{C_p}{C_v} \\ a &= \sqrt{R_g T \gamma} \end{aligned} \tag{15}$$

$$\begin{aligned} C_{v,e} &= C_{p,e} + \frac{R_g \left(\frac{\delta \ln V}{\delta \ln T}\right)_P^2}{\left(\frac{\delta \ln V}{\delta \ln P}\right)_T} \\ \gamma_s &= -\frac{\gamma}{\left(\frac{\delta \ln V}{\delta \ln P}\right)_T} \\ a_e &= \sqrt{R_g T \gamma_s} \end{aligned} \tag{16}$$

Equilibrium properties during a phase change between condensed species

As was explained by Gordon (1971), during the transition between condensed phases, at which temperature stays constant, derivatives with respect to temperature are not properly defined. Therefore, expressions such as Eq. 16 cannot be used. Gordon presents an alternative definition for the isentropic isothermal case:

$$\gamma_{S,T} = -\frac{1}{(\ln V/\ln P)|_T}$$
$$a_e = \sqrt{R_g T \gamma_{S,T}} \tag{17}$$

Note that this definition change will cause a notable discontinuity in the values of gamma and the speed of sound. It is also important to point out that, as was explained in prior sections, the value for R_g needs to account for the presence of condensed species.

In this isothermal region, the equilibrium values for C_p and C_v are not defined. Therefore, only their frozen counterparts can be used, and the ODEKO software only offers frozen variables as output for this region. Note as well that, even if equilibrium variables present a discontinuity at the start and end of the isothermal region, frozen variables are always continuous (although some show a discontinuity in their first derivative). This is the case as frozen variables represent a physical quantity (which cannot be discontinuous), whilst equilibrium variables are a tool to show the effect of the chemical reactions taking place.

Transport properties

The viscosity is computed equally for frozen and equilibrium flow, not having a dual definition like the other variables. On the other hand, the conductivity requires a kinetic scheme to be specified for its computation. The reacting component of the conductivity, as shown by Gordon and McBride (1994) can be computed as:

$$\sum_{j=1}^{NK} \tau_{ij}\lambda_{r,j} = \frac{\Delta H_i^o}{RT} \qquad (i = 1, ..., NK) \tag{18}$$

Where ΔH^o corresponds to the net enthalpy variation of reaction i and τ_{ij} is given by:

$$\tau_{ij} = \sum_{k=1}^{NT}\sum_{l=k+1}^{NT}\left(\frac{RT}{PD_{kl}}x_k x_l\right)\left(\frac{\upsilon_{ik}}{x_k} - \frac{\upsilon_{il}}{x_l}\right)\left(\frac{\upsilon_{jk}}{x_k} - \frac{\upsilon_{jl}}{x_l}\right) \tag{19}$$

The value of υ_{ik} corresponds to the net coefficients of specie k in reaction i and ${}^{RT}PD_{kl}$ equates to:

$$\frac{RT}{PD_{kl}} = \frac{5\mathcal{M}_k\mathcal{M}_l}{3A^*_{kl}\mu_{kl}(\mathcal{M}_k + \mathcal{M}_l)} \tag{20}$$

One-dimensional equilibrium (ODE) in rocket engines

The first step to solve the flow through the nozzle is to calculate the equilibrium composition at the combustion chamber (constant enthalpy). The enthalpy of the reactants is easily obtained, since their starting temperature is given by the user or the database. The chamber pressure is also given. Therefore, the composition at the combustion chamber is obtained without any complications. Subsequently, the composition and thermodynamic properties of the nozzle's throat are to be computed. The convergence criterion is:

$$\left|\frac{v_t^2 - a_{e,t}^2}{u_t^2}\right| \leq 0.4 \cdot 10^{-4} \tag{21}$$

Note that this condition implies that the Mach number is unity at the throat. For 1D chemical equilibrium, this is only true if the speed of sound considered is the equilibrium speed of sound.

Once the throat has been calculated, the rest of the points of the nozzle are computed in the same manner. Firstly, an initial estimate for the pressure is obtained and, afterward, the value for the pressure is iterated according to the following formula, employed by Gordon and McBride (1994):

$$\left(\ln\frac{P_{inf}}{P}\right)^{(k+1)} = \left(\ln\frac{P_{inf}}{P}\right)^{(k)} + \left(\frac{\delta\ln\frac{P_{inf}}{P}}{\delta\ln\frac{A}{A_t}}\right)_s \cdot \left[\ln\frac{A}{A_t} - \ln\frac{\rho_t u_t}{\rho u}\right] \tag{22}$$

Where the partial derivative can be expressed as:

$$\left(\frac{\delta\ln\frac{P_{inf}}{P}}{\delta\ln\frac{A}{A_t}}\right)_s = \left(\frac{\gamma_s u^2}{u^2 - a^2}\right) \tag{23}$$

After all points have been computed (equilibrium composition along with thermodynamic and transport variables if requested), the rocket parameters may be calculated as well, employing the following equations:

$$\begin{aligned} E &= \dot{m}v_{exit} + (P_{exit} - P_a)A_{exit} \\ I_{sp} &= \frac{E}{\dot{m}} \\ c^* &= \frac{P_{inf}A_t}{\dot{m}} \\ C_E &= \frac{I_{sp}}{C*} \end{aligned} \tag{24}$$

The mass flow is computed at the throat. Even though it should be constant along the nozzle, very small variations are present due to the nature of the numerical method. Since all points are calculated, establishing that their mass flow should equal that of the throat, it is regarded as the most representative value.

Frozen flow

If the flow is set to "freeze" (stop reacting) after the throat, the procedure is simple, as shown by Gordon and McBride (1994). After the frozen point, composition is conserved and the iteration procedure remains the same. Since the equilibrium equations can no longer be used, the temperature of the mixture must also be iterated (for each pressure iteration there must be a temperature convergence). The iteration is performed using the constant entropy condition (non-viscous, non-reacting flow with no heat transfer), as shown in Eq. 25:

$$(\ln T)^{(k+1)} = (\ln T)^{(k)} + \frac{s_{inf} - s}{C_{p,f}} \tag{25}$$

The convergence condition is:

$$\left|\frac{s_{inf} - s}{C_{p,f}}\right| \leq 0.5 \cdot 10^{-4} \tag{26}$$

On the other hand, if the freezing point is located before the throat, an additional iteration procedure for the throat is required. To calculate the parameters of the freezing point (especially its pressure, required to obtain its composition), the throat must be computed first. The only option is to calculate the throat in its equilibrium condition. Once the frozen point is computed, the throat can be recalculated with the frozen composition. One should note that this will fundamentally change the parameters of the nozzle's throat. Therefore, the freezing point will no longer be correctly computed (it will not be coherent with the new throat values). Consequently, this process is iterated until the freezing point and throat are compatible. To the knowledge of the authors, no other freely available software gives the user the option to freeze the composition before the throat.

Note that this process usually requires many iterations. Despite this, it is still relatively fast, since only two points are being computed back and forth. Generally, frozen flow is much faster to compute in spite of the additional iteration procedure required. Note as well that, once the flow freezes, all parameters used must also be "frozen". In consequence, equilibrium variables can no longer be used for any iteration or convergence criterion, since the flow is no longer in chemical equilibrium.

Convergence criteria during isothermal regions caused by transitions between condensed phases

If the throat of the nozzle is contained at the start of the isothermal region of a condensed phase transition, it results in a discontinuity of the speed of sound at the throat, as described by Eq. 17. According to the indications of Gordon (1971), the following criterion should be used:

$$\ln {P_t}^{k+1} = \ln {P_t}^{k} + \left(\frac{\delta \ln P}{\delta \ln T}\right)_S (\ln T_m - \ln T) \tag{27}$$

Where T_m is the phase transition temperature between both phases and T is the temperature of the mixture. The derivative value can be expressed as:

$$\left(\frac{\delta \ln P}{\delta \ln T}\right)_S = \frac{c_P}{R_g \left(\frac{\delta \ln V}{\delta \ln T}\right)_P} \tag{28}$$

RESULTS

The parameters of the arbitrary parabolic nozzle employed in the subsequent sections are shown in Tables 1 and 2. The employed propellants will be referred to as liquid hydrogen and liquid oxygen (LHLO) with O/F = 5, nitroglycerin to nitrocellulose (NCNG) ratio of 10, ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) with O/F = 4, and potassium nitrate and sorbitol (RC) with O/F = 65/35. Chamber pressure is 3 MPa for all configurations unless stated otherwise.

Table 1. Main nozzle parameters.

Entrance diameter	0.5 m
Throat diameter	0.25 m
Exit diameter	1 m
Convergent length	0.5 m
Divergent length	1 m

Source: Elaborated by the authors.

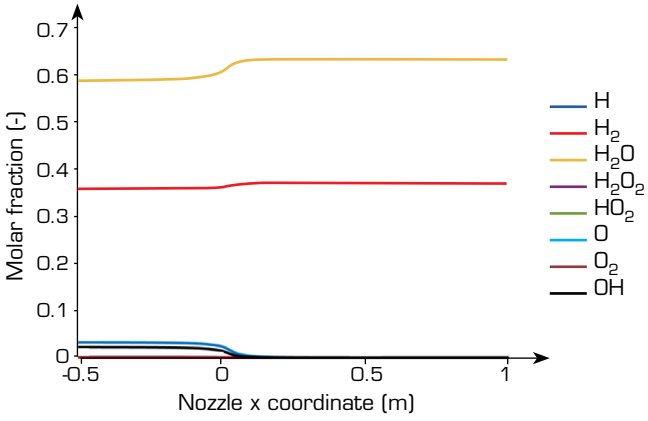
Table 2. Additional nozzle parameters.

Initial parabola angle	50°
Final parabola angle	5°
Entrance fillet radius	0.1 m
Convergent throat fillet radius	0.1875 m
Divergent throat fillet radius	0.04775 m

Source: Elaborated by the authors.

Chemical equilibrium results

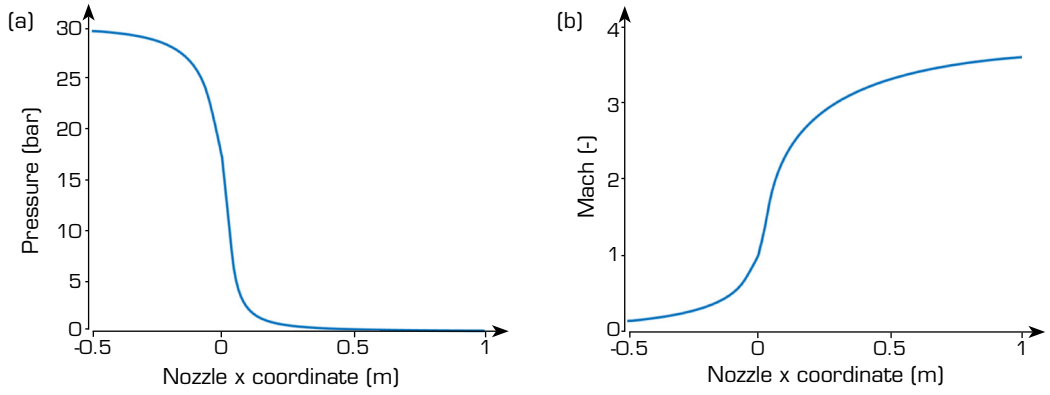
As an example, a simulation using LHLO and the specified nozzle will be performed. In Fig. 1, the evolution of the different species is shown. The composition remains fairly similar in the regions far away from the throat. Near the throat, a depletion of H and OH (as well as O and O_2, even though it is not visible in the plot) results in an increase of the molecular fractions of H_2O and H_2. Note that, for a mix of hydrogen and oxygen at the given pressure and temperature conditions, there are very few relevant species involved, greatly simplifying the calculations. Nevertheless, for other propellant types with a greater variety of chemical elements, a significant amount of chemical species play an important role in the determination of chemical equilibrium, leading to more complex systems.



Source: Elaborated by the authors.

Figure 1. Evolution of composition along the nozzle for LHLO.

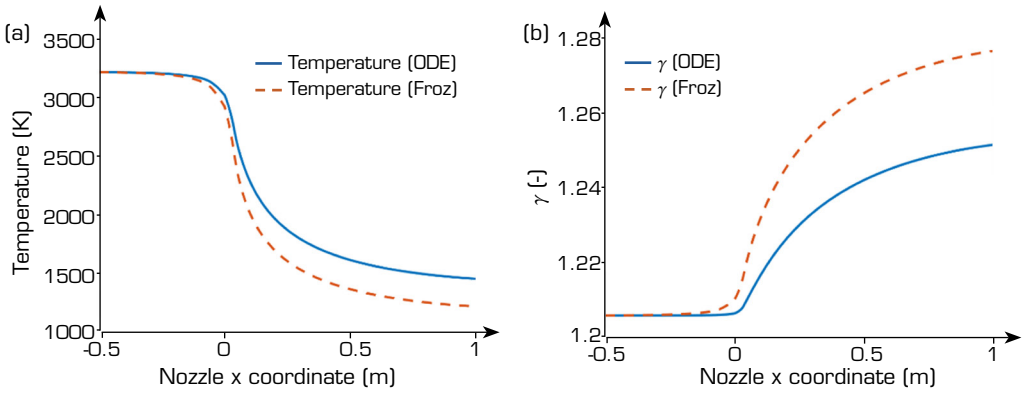
The gradient in pressure is largest near the throat, as seen in Fig. 2a. On the other hand, the gradient in Mach number peaks after the throat, with a Mach number of 1 at the throat itself, as shown in Fig. 2b. The strong pressure gradient near the throat,



Source: Elaborated by the authors.

Figure 2. Evolution of pressure and Mach number along the nozzle for LHLO. (a) pressure evolution; (b) Mach evolution.

as well as the temperature gradient shown later in Fig. 3a, explain the shift in composition seen in this region in Fig. 1. It is of mention that the pressure evolution is barely impacted by the shift in composition, leading to very close results between the chemical equilibrium and frozen computations. On the contrary, other variables show a significant difference in value based on whether chemical reactions have been accounted for or not, as will be shown in detail in the next subsection.

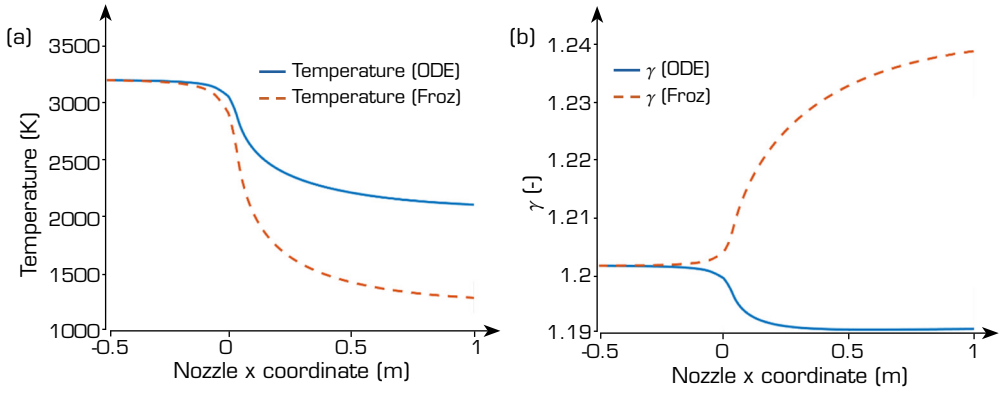


Source: Elaborated by the authors.

Figure 3. LHLO. (a) Temperature evolution; (b) gamma evolution.

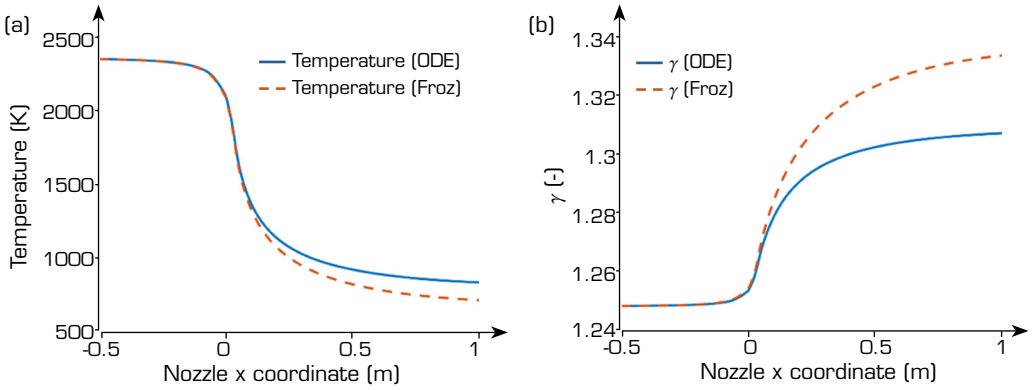
Comparison of ODE and frozen flow

A comparison between flow through the nozzle computed with chemical equilibrium and "freezing" said flow at the throat is given for a series of propellants, shown in Figs. 3–5. The flow temperature throughout the nozzle is higher when chemical equilibrium is considered. This is a consequence of exothermic reactions occurring throughout the nozzle, initiated by the decrease in pressure and temperature. On the other hand, the frozen value for gamma tends to be lower. The real performance (finite reaction rates) will sit somewhere between the frozen (no reaction) and equilibrium (infinitely fast reaction rates) limits, depending on the speed of the reactions for the given parameters and propellant. Slow-reacting propellants such as AP/HTPB are typically better modeled by freezing the flow at the throat, whilst faster-reacting propellants like LHLO are better predicted using chemical equilibrium. For the LHLO case, shown in Fig. 3, the results of the frozen and equilibrium calculations start to differ slightly before the throat. This is coherent with Fig. 1, as it is where the composition starts to vary in the chemical equilibrium computations. On the other hand, for the NCNG case and, especially, for AP/HTPB, this deviation starts to happen at a later point of the nozzle, caused by the different evolution of the chemical composition for these propellants.



Source: Elaborated by the authors.

Figure 4. NCNG. (a) temperature evolution; (b) gamma evolution.

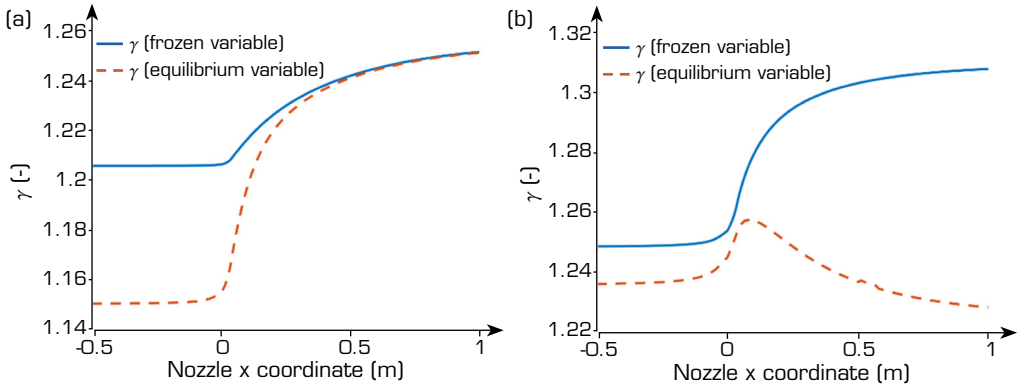


Source: Elaborated by the authors.

Figure 5. AP/HTPB. (a) temperature evolution; (b) gamma evolution.

Frozen and equilibrium variables

In this section, the entire flow is computed using chemical equilibrium, and the frozen and equilibrium values of gamma are compared. It is notable that, for the LHLO propellant (Fig. 6a), the frozen and equilibrium gammas tend to the same value as the exit area increases (due to reactions halting). On the other hand, for AP/HTPB (Fig. 6b), the frozen and equilibrium values differ more and more with increasing exit area (as a consequence of substantially different compositions at this point).



Source: Elaborated by the authors.

Figure 6. Comparison of equilibrium and frozen variables for equilibrium calculations. (a) gamma evolution for LHLO; (b) gamma evolution for AP/HTPB.

Transition between condensed phases

In this section, the propellant RC is used to showcase the transition between condensed phases in the nozzle. In Fig. 7a, it is apparent that the equilibrium flow has an isothermal region in the nozzle, corresponding to the phase transition. On the other hand, the flow frozen at the nozzle throat does not experience said transition and has a more typical temperature curve. In Fig. 7b, the composition of both condensed species is shown for the flow computed with chemical equilibrium.

In addition, for a flow computed fully with chemical equilibrium, there are two possible ways to compute variables such as the speed of sound. Said approaches are referred to as "frozen" and "equilibrium" variables, as previously presented in Eqs. 15 and 16. Both types of variables for the example with condensed phases are compared in Fig. 8. It is crucial to note that, although referred to as "frozen" and "equilibrium" variables, both are obtained from an equilibrium computation. This illustrates the discontinuity present in the value of the equilibrium variables, as mentioned in prior sections. Moreover, it can be seen that the frozen value for gamma and, especially, that of the speed of sound have a discontinuity in their first

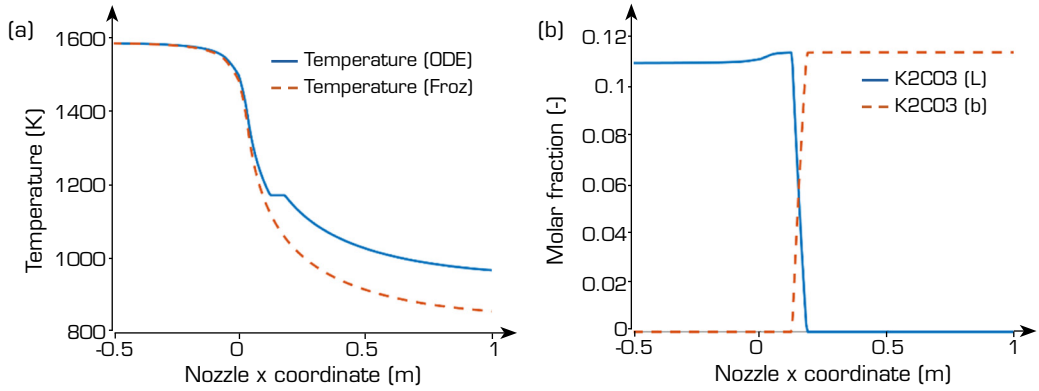


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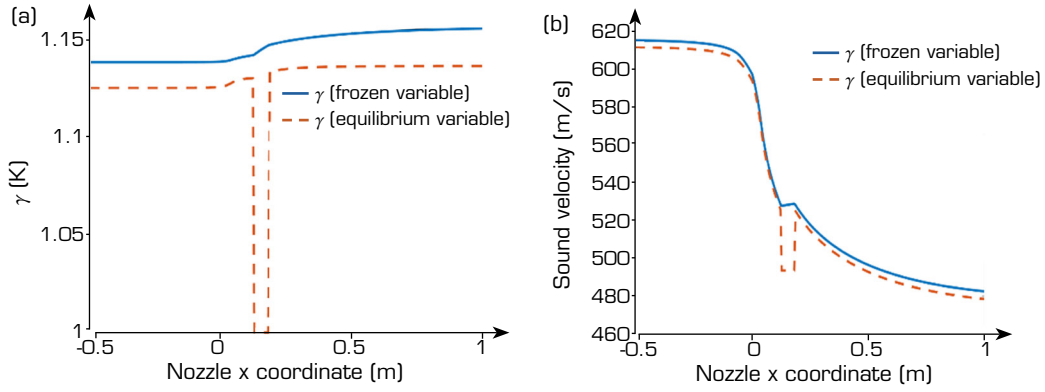
Figure 7. Transition between condensed phases. (a) temperature evolution for equilibrium and frozen calculation; (b) composition evolution for equilibrium calculation.



Source: Elaborated by the authors.

Figure 8. Comparison of frozen and equilibrium variables during a transition between condensed phases. (a) frozen and equilibrium gamma values for equilibrium calculations; (b) frozen and equilibrium sound velocity value for equilibrium calculations.

derivative at the entrance and exit of the isothermal region. It is also notable that the equilibrium gamma is very close to 1 (around 0.9996) throughout the isothermal region. A value of 1 is intuitively reasonable, as the addition of heat at constant pressure and constant volume results in the same temperature change (none, as only the composition changes during a phase change). Therefore, the values of c_p and c_v should be equal to each other in this example. In spite of this, the reader must keep in mind that the values of c_p and c_v are not properly defined in this case. Furthermore, the frozen speed of sound increases in value during the isothermal region. This is easily explained, given that the temperature remains constant whilst the frozen gamma is increasing.

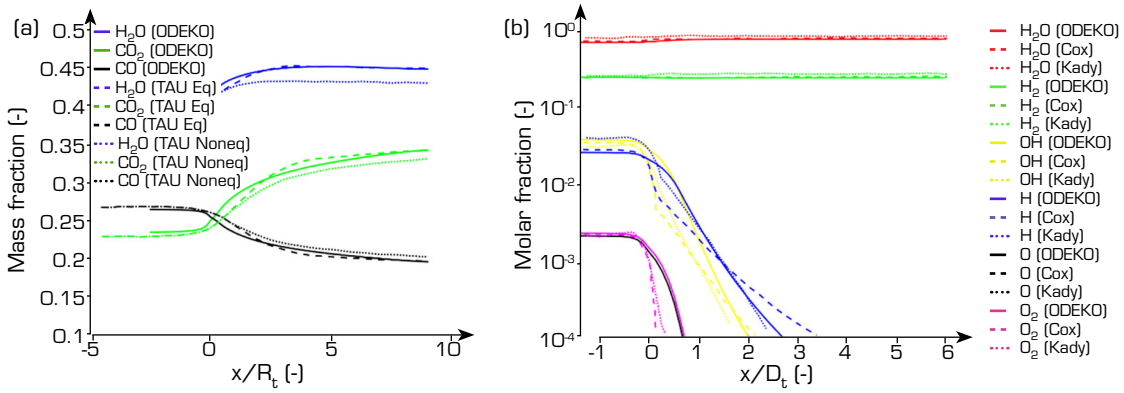
Validation against multidimensional and turbulent simulations

There are multiple physical effects that are not modeled by ODEKO. The simulation performed by ODEKO is strictly 1D for the nozzle, leaving out divergence effects. The combustion chamber is modeled as 0D, resulting in turbulence, mixing, injection, and atomization effects not being accounted for. Turbulence, as well as viscosity, is not modeled anywhere in the entire system. Heat losses are also disregarded, as the entire system is considered adiabatic.

In this section, it will be shown that, even with the aforementioned limitations, ODEKO offers very similar results to much more complex and detailed CFD simulations that do consider these effects, but at a fraction of the computational cost. This is expected, as ODEKO considers the most relevant aspects of the flow. It only leaves out the modeling aspects, which, although relevant for detailed design, do not contribute much to the behavior of the entire system.

Firstly, a RANS simulation of a methane-oxygen rocket engine performed by DLR's (German Aerospace Center) in-house code TAU is used to validate the results of the developed software, ODEKO. The simulation was performed by Schneider and Génin (2017), corresponding to real engine operation conditions, as reported in Burkhardt and Sippel (2004). As the pressure used in the simulation was not stated, a value of 40 bar was assumed based on the experimental data provided. The 2D axially symmetric RANS simulation by Schneider and Génin (2017) results are provided both for the chemical equilibrium and nonequilibrium (finite-rate chemistry cases).

In Fig. 9a, the equilibrium and nonequilibrium results along the centerline of the 2D TAU simulation are compared with the 1D results obtained by ODEKO. There is a good match in results between ODEKO and the chemical equilibrium TAU simulation. Note that, even though the TAU chemical equilibrium simulation considers turbulence (RANS) and is 2D, there is no significant difference in results with the much simpler and computationally cheaper ODEKO simulation. The differences in the shape of the curves can be attributed to the assumptions made about the nozzle shape, as only the entrance, throat, and exit areas were reported by Schneider and Génin (2017), as well as to the fundamental differences between 2D and 1D codes.

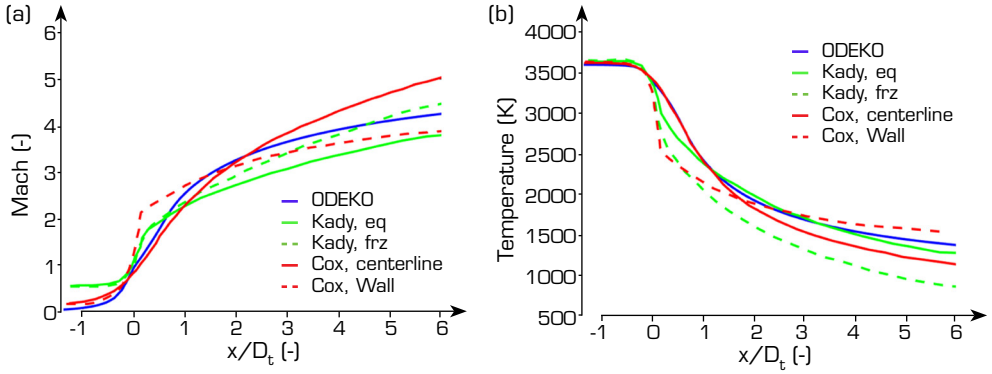


Source: Elaborated by the authors, using data from Schneider and Génin (2017).

Figure 9. Comparison of mixture evolution for two validation cases. (a) mixture evolution of DLR's example case nozzle; (b) mixture evolution of the SSME nozzle.

Next, the Space Shuttle Main Engine Nozzle will be simulated with the developed software, ODEKO, and compared to the results obtained by Al Kady (2013). The SSME employs LHLO as propellant. The work by Al Kady (2013) consists of an LES using both the $k-\omega$ and $k-\varepsilon$ models, based on the distance to the nozzle walls. Al Kady (2013) performed a 2D axisymmetric simulation, assuming the flow to be in chemical equilibrium at every grid point of the domain. In the work by Al Kady (2013), the results are also compared and shown to match with the ones obtained by Cox and Cooper (1994), which will also be used in the subsequent comparison. Cox and Cooper (1994) use a 2D-axisymmetric Riemann solver with chemical equilibrium for their simulations.

A comparison of the mixture evolution is provided in Fig. 9b. A very good match between ODEKO and both validation sources is seen for H_2O and H_2, and a good match with Al Kady (2013) and decent with Cox and Cooper (1994) for OH. The largest difference in results corresponds to O and O_2, where ODEKO predicts the drop-off in composition slightly afterwards in the axial direction. Note that neither paper presents the exact nozzle curve employed; therefore, an assumption was required, which might explain differences observed in the divergent region of the nozzle. Nevertheless, the match is quite good considering the additional complexity of a 2D LES. The Mach evolution is shown in Fig. 10a and the temperature evolution in Fig. 10b. It is of note that the prediction by ODEKO mostly stays between the wall and centerline values for Cox, which is a positive sign, given the dimensional difference. The temperature predicted by ODEKO matches well with the equilibrium simulation by Al Kady (2013), although the Mach number is not as accurately matched. The specific impulse was compared to the one reported by NASA in Van Hooser (2011). ODEKO gives a value of 465 s, whilst NASA reports a real value of 452 s. Given that ODEKO does not account for turbulent, viscous, divergence, heat transfer, or nonequilibrium losses, this result, with less than a 3% error, is extremely good.



Source: Elaborated by the authors, using data from Al Kady (2013) and Cox and Cooper (1994).

Figure 10. Evolution of key variables throughout the SSME's nozzle. (a) Mach; (b) temperature.

Input and output of ODEKO

The developed software, ODEKO, comes equipped with a large database of reactants and species to be included in the chemical equilibrium calculations. The user can choose from this database to select which reactants form their propellant and which species should be considered for the computations. Furthermore, the user also has the option to include additional reactants or species if so desired.

Once the propellant is defined, the user should specify the nozzle's main parameters (entrance, throat, and exit areas) as well as its shape. The only other input required is the chamber pressure. For solid rocket motors, instead of the chamber pressure, the grain geometry and its Vielle parameters should be specified instead. Almost all other parameters involved in the calculation process can be modified from the preferences menu. Nevertheless, suitable values are set by default, making it unnecessary to change any of them.

The outputs provided by ODEKO, at the combustion chamber and all points of the nozzle, include:

- Chemical composition – of all species involved in the calculation.
- Thermodynamic properties – pressure, temperature, density, enthalpy, entropy, mixture molecular weight, gamma, velocity, speed of sound, Mach, C_p, and C_v.
- Transport properties – conductivity, viscosity, convective heat transfer coefficient, and Prandtl number.

Additionally, the following rocket engine properties are also reported: combustion temperature, thrust (at a given ambient pressure), specific impulse, $C*$, $C_{E,}$ and mass flow, as well as chamber pressure and combustion time for solid rocket motors.

DISCUSSION

The present work brings a revision and update to previously existing algorithms, integrated into novel software for general-purpose low-order simulation of the internal flow of rocket engine nozzles. A notable addition with respect to previously existing software is the introduction of a method to freeze composition changes at any specific point within the nozzle, allowing customized modeling for realistic engine conditions. Furthermore, the ability to show both the frozen and equilibrium values of a variable when a chemical equilibrium calculation is performed offers much greater versatility and control to the user.

CONCLUSIONS

In the field of rocket engine design and analysis, the calculation of performance along the nozzle's equilibrium composition plays a pivotal role. This study has emphasized the importance of this approach, showcasing its significance in comprehending and optimizing the performance of thermochemical rocket engines. The inclusion of calculations for both gaseous and condensed species has allowed

for a comprehensive analysis of engine behavior. The introduction of the capability to freeze composition at specific nozzle points adds a valuable dimension. It enables tailored modeling to match real-world engine conditions, thereby enhancing its versatility as an analysis and design tool. Additionally, the study's calculation of transport properties along the nozzle has further enriched the depth of our understanding. By integrating equilibrium composition, condensed species, and transport properties, this research demonstrates a holistic approach to analyzing and optimizing thermochemical rocket engine performance. The inclusion of multiple illustrative examples, as well as validation against 2D RANS and LES simulations, serves to underscore the practical capabilities of the program. This makes it a valuable resource for researchers, engineers, and scientists in the aerospace industry.

The software ODEKO is open-access and can be freely downloaded from www.odeko.nickdejongc.com.

CONFLICT OF INTEREST

Nothing to declare.

AUTHORS' CONTRIBUTION

Conceptualization: Pulido JMT; **Data Curation:** Cantariño NJ; **Formal Analysis:** Cantarino NJ; **Funding Acquisition:** Pulido JMT; **Investigation:** Cantariño NJ and Pulido JMT; **Methodology:** Cantariño NJ and Pulido JMT; **Project Administration:** - ; **Resources:** Pulido JMT; **Software:** Cantariño NJ; **Supervision:** Pulido JMT; **Validation:** Cantariño NJ and Pulido JMT; **Visualization:** Cantariño NJ; **Writing:** Cantariño NJ and Pulido JMT; **Review:** Cantariño NJ and Pulido JMT; **Final approval:** Cantariño NJ.

DATA AVAILABILITY STATEMENT

All data sets were generated or analyzed in the current study.

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