



HAL
open science

A revised model of ammonium perchlorate combustion with detailed kinetics

Pierre Bernigaud, Dmitry Davidenko, Laurent Catoire

► **To cite this version:**

Pierre Bernigaud, Dmitry Davidenko, Laurent Catoire. A revised model of ammonium perchlorate combustion with detailed kinetics. *Combustion and Flame*, 2023, 255, pp.112891. 10.1016/j.combustflame.2023.112891 . hal-04148974

HAL Id: hal-04148974

<https://hal.science/hal-04148974>

Submitted on 3 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

A Revised Model of Ammonium Perchlorate Combustion with Detailed Kinetics

Pierre Bernigaud^{a,†}, Dmitry Davidenko^a, Laurent Catoire^b

^a DMPE, ONERA, Université Paris Saclay, 91120 Palaiseau, France

^b Unité Chimie et Procédés (UCP), ENSTA Paris, Institut Polytechnique de Paris, 91120 Palaiseau, France
pierre.bernigaud@onera.fr · dmitry.davidenko@onera.fr · laurent.catoire@ensta-paris.fr

[†]Corresponding author

Abstract

In this study, we propose a revised coupled combustion model for ammonium perchlorate (AP), leveraging recent advances in the modelling of ammonia and NO_x chemistry. A coupled combustion model relies on three founding bricks: a detailed gas-phase kinetic model, a condensed-phase decomposition model, and a pyrolysis law describing the relationship between the surface temperature and mass flow. The proposed gas-phase kinetic model, is validated against data on species sampling in jet-stirred reactors, laminar flame speed, and ignition delay time. These test cases, rarely used by the solid propellant community, highlight deficiencies in a reference mechanism from the literature. A new model for AP decomposition in the condensed phase is proposed to be used with the gas-phase mechanism. A suitable pyrolysis law is designed using the Zel'dovich-Novozhilov theory to ensure the stability of the coupled combustion model. The methodology employed is described in detail, for others to replicate. Finally, the overall model is applied to simulate the AP laminar flame in a 1D coupled approach. These calculations provide results on the regression rate, surface temperature, temperature sensitivity and species profiles for prescribed initial temperature of AP and ambient pressure. The behavior of the proposed combustion model is presented in comparison with other reference models. The role of gas-phase kinetics in modeling AP combustion is discussed.

Keywords: Ammonium perchlorate; kinetic mechanism, pyrolysis law; coupled flame/solid simulation

1 **1. Novelty and Significance**

2 Current models for ammonium perchlorate (AP) combustion have been used for more than a decade without
3 significant revision or improvement. Furthermore, all of these models have been validated primarily on a dataset
4 limited to AP combustion with a unique case of detailed flame structure. By applying a more rigorous method-
5 ology, the validation dataset is expanded adding cases on simple reactive systems of interest. This approach
6 highlights fundamental deficiencies in the mechanisms which were widely used in the past. A new gas-phase
7 kinetic mechanism with improved confidence is assembled and validated on the expanded dataset. A condensed-
8 phase decomposition model is formulated to be used conjointly. Finally, a pyrolysis law is designed employing the
9 Zel'dovich-Novozhilov theory of solid propellant combustion stability and optimizing the Arrhenius parameters.

10 **2. Authors Contributions**

12 P. B. performed research, wrote the paper.
13 D. D. supervised research, wrote the paper.
14 L. C. supervised research.

15 **3. Introduction**

17 Ammonium perchlorate combined with a polymeric binder such as hydroxytelechelic polybutadiene (HTPB)
18 is a widely used ingredient for composite solid propellants. These composite propellants are used for both civil-
19 ian and military applications. While the binder provides the combustible gases via its pyrolysis, the AP acts as
20 a source of oxidizer. The combustion process is controlled by the modal distribution of the AP particles in the
21 propellant. A composite propellant can be tailored to meet specific requirements using appropriate AP loading.
22 In order to design a composite propellant, it is important to understand and properly model the combustion of pure
23 AP. To this end, it is necessary to develop a detailed chemical kinetic mechanism in the gas phase and a model of
24 AP decomposition in the condensed phase.

25 Extensive experimental work has been carried out in the past, the results of which are essential for the construc-
26 tion and validation of numerical models. The models must first verify the macroscopic characteristics of the AP
27 combustion: Atwood and Boggs [1] measured the regression rate of AP at various pressures, as well as the initial
28 temperature sensitivity. Surface temperature measurements were performed by Bakhman et al. [2], Powling et al.
29 [3], and Korobeinichev et al. [4]. The combustion model must also represent the underlying chemical mechanisms
30 within the flame. To this end, the work of Ermolin et al. [5] provides chemical species profiles in an AP flame at
31 low pressure. For this same flame, Tereshenko et al. [6] reported measurements of the temperature profile near the
32 regression surface. On this experimental base, Ermolin et al. [5] proposed a first chemical kinetic mechanism in
33 the gas phase, able to reproduce satisfactorily the measured species profiles. Tanaka et al. [7] then Jing et al. [8]
34 presented models coupling the gas-phase combustion and condensed-phase decomposition processes. The inclu-
35 sion of the condensed phase has improved the macroscopic performance of the model (prediction of burning rate,
36 temperature sensitivity). Efforts to develop more accurate combustion models for AP were continued by Meynet
37 et al. [9], Gross et al. [10] and Smyth et al. [11].

38 Ammonium perchlorate (NH_3HClO_4) decomposes in the condensed phase via different pathways, the most impor-
39 tant of them forming NH_3 and HClO_4 . The presence of NH_3 among the main decomposition products requires an
40 appropriate kinetic model for NH_3 , its subsequent radicals, and NO_x . Chemical experiments involving ammonia
41 have been numerically reproduced with the model used by Gross et al. [10], highlighting some important deficien-
42 cies.

43 Based on this finding, we first propose a new gas-phase kinetic model for AP combustion based on the recent work
44 on ammonia oxidation from Shrestha et al. [12]. A revised model of the condensed-phase decomposition process
45 is then formulated to be coupled to the new gas-phase kinetic mechanism. The relation between the regression
46 rate and the surface temperature is specified via an adapted pyrolysis law. Simulations of AP combustion using
47 a coupled flame/solid approach are performed to evaluate several macroscopic parameters (burning rate, surface
48 temperature), serving as validation criteria with respect to the available experimental data. Temperature and chem-
49 ical species profiles are computed for the low-pressure flame studied by Ermolin et al. [5] and Tereshenko et al.
50 [6]. Finally, a stability study is carried out, in the sense of the Zel'dovich-Novozhilov theory [13].

51 **4. Gas Phase Mechanism**

53 The proposed mechanism for AP combustion consists of 36 species and 205 reactions. It contains sub-mechanisms
54 for the H-O system, nitrogen-containing species, and chlorinated species. This model was developed based on the
55 work of Shrestha et al. [12] on ammonia combustion for the H-O-N part of the mechanism. This reference model
56 is hereafter called the Shrestha model. The choice of this specific mechanism for the reactions involving NH_3 and

57 other nitrogen-containing species is based on its validation against a large data-set. It is to be noted that ammonia
 58 combustion is still a very active field of research, and more recent mechanisms can be found, see Shrestha et
 59 al. [14], Baker et al. [15]. The sub-mechanism for chlorinated species is inspired by the work of Smooke and
 60 Yetter [16], itself based on the historic mechanism proposed by Ermolin et al. [17]. This last sub-mechanism also
 61 includes reactions used by Pelucchi et al. [18] in his study of the HCl/Cl₂ chemistry at high temperature. The
 62 proposed mechanism is available in the supplementary materials.

63 In the following subsections, the ability of the mechanism to accurately represent the NH₃/O₂ chemistry is first
 64 validated via laminar flame speed and ignition delay calculations. The H₂/O₂/NO_x chemistry is tested on experi-
 65 ments in a jet-stirred reactor and a shock tube. The correct treatment of the Cl₂/H₂ chemistry is also verified via
 66 laminar flame speed and ignition delay calculations. The test cases are selected from the works of Shrestha et al.
 67 [12] and Pelucchi et al. [18]. This is to ensure that the performance of the assembled AP kinetic model is similar
 68 to the original mechanisms from [12, 18]. The results presented below serve to demonstrate AP model improve-
 69 ments with respect to existing AP mechanisms, and not to provide an exhaustive validation. The new mechanism
 70 is compared to the reference model proposed by Gross et al. [10], hereafter called the Gross model (25 species,
 71 80 reactions). This specific model is chosen as a reference, owing to its frequent usage within the solid propellant
 72 community.

73 Chemical experiments are simulated employing the Cantera software [19]. Laminar flame speed is obtained under
 74 the hypothesis of adiabatic combustion. Jet-stirred reactors are modeled as perfectly-stirred reactors. In order to
 75 assess the performance of a given kinetic model, we use the adimensional L_2 error norm:

$$\delta_{err} = \frac{1}{\mu_y} \left[\sum_{k=1}^N (y_k - \hat{y}_k)^2 \right]^{\frac{1}{2}} \quad (1)$$

76 Where N is the number of experimental data points, the k -th data point is (x_k, y_k) , \hat{y}_k is the estimate produced
 77 by a model at x_k , and μ_y is the average value of the experimental data points. For ignition delay experiments, the
 78 log-ratio measure is used to better represent the large range of time scales within the data:

$$\delta_{err} = \left[\sum_{k=1}^N \left(\log \frac{y_k}{\hat{y}_k} \right)^2 \right]^{\frac{1}{2}} \quad (2)$$

79 Where \log is the decimal logarithm.

80 4.1. NH₃ / O₂ Chemistry

81 Ammonia (NH₃) is one of the main decomposition products of ammonium perchlorate. In order to validate the
 82 oxidation sub-mechanism of NH₃, different experiments are reproduced with the present model. The ignition delay
 83 time for a highly diluted NH₃/O₂ mixture is calculated for various pressure and equivalence ratio. The results are
 84 compared in Figure 1 with the measurements in shock-tube experiments by Mathieu et al. [20]. The error between
 85 the model predictions and experimental data is quantified in Table 1.

Table 1: Ignition delay time for NH₃/O₂ mixtures: error norm of the model predictions.

ϕ	P (atm)	δ_{err}
0.5	1.4	$2.69 \cdot 10^{-1}$
0.5	11	$1.94 \cdot 10^{-1}$
0.5	30	$1.48 \cdot 10^{-1}$
1	1.4	$3.55 \cdot 10^{-1}$
1	11	$2.07 \cdot 10^{-1}$
1	30	$1.95 \cdot 10^{-1}$

86 Good agreement between the model predictions and the experimental results is achieved. Results obtained with the
 87 Gross model [10] are not reported: no ignition was observed with it. Indeed, this model has no reaction between
 88 NH₃ and O₂, nor dissociation reaction for these species. The ignition is initiated in the present mechanism via
 89 reactions R92 and R97:



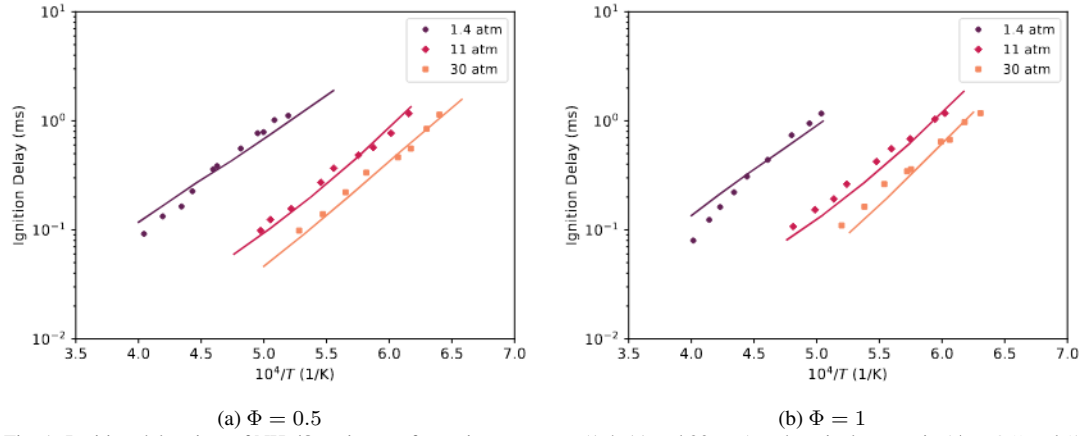


Fig. 1: Ignition delay time of NH_3/O_2 mixtures for various pressure (1.4, 11 and 30 atm) and equivalence ratio ($\phi = 0.5$ and 1), initial temperature 298 K. Symbols: experiment [20]. Lines: model predictions.

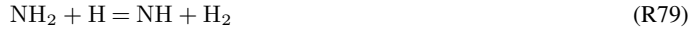
90 Reaction R92 is particularly important. It produces hydrogen atoms, which participate in the formation of the OH
 91 and O radicals via the following reaction:



92 The ammonia NH_3 is then transformed into NH_2 by reactions with O, H and OH radicals:



93 Reactions R93 and R94 consume the majority of NH_3 . NH_2 is then converted via two paths, forming NH and
 94 N_2H_2 respectively:



95 The final product N_2 is mainly formed from N_2H_2 via the intermediary NNH:



96 Several hydrogen-abstraction reactions involving NH_x produce H_2 , which is finally converted into H_2O via:



97 The predicted laminar flame speeds for the NH_3 / air system at 1 atm are presented in Figure 2a and compared
 98 with available experimental data. Are also reported the predictions obtained with the Gross reference model [10]
 99 and the Shrestha model [12] that served for the development of the present work. The error norm related to each
 100 model is presented in Table 2.

101 Good agreement is found between the predictions of the present model and the experimental results. The Gross
 102 model [10] over predicts the flame speed, especially at lower equivalence ratios but captures the velocity maximum

Table 2: Laminar flame speed for NH₃/ air mixtures at 1 atm: error norm of the model predictions.

Model	δ_{err}
This work	$1.94 \cdot 10^0$
Shrestha [12]	$2.07 \cdot 10^0$
Gross [10]	$2.14 \cdot 10^1$

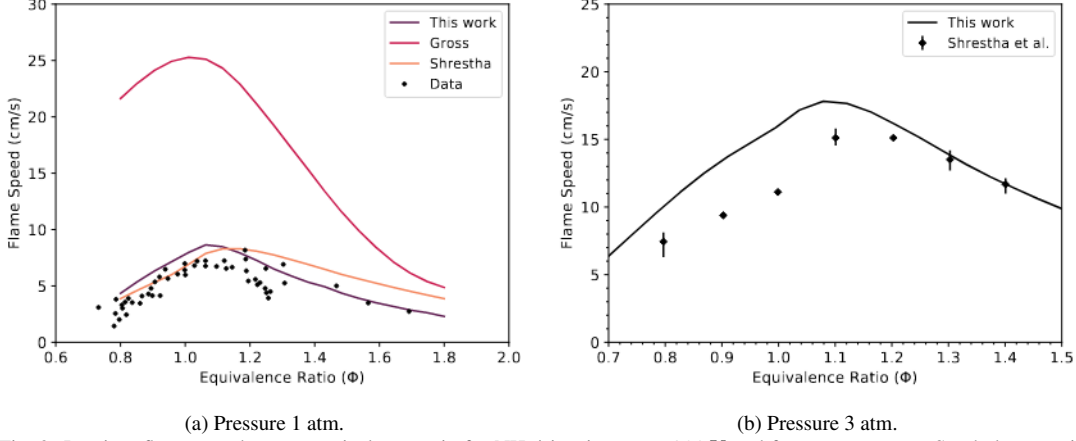


Fig. 2: Laminar flame speed versus equivalence ratio for NH₃/air mixtures at 298 K and for two pressures. Symbols: experiments. (a) [21–26], (b) [14]. Lines: Model predictions.

around stoichiometry. It may be noted that the present mechanism performs better than the Shrestha model [12] for rich conditions, where the slope defined by the experimental points is well followed. To test the mechanism at a higher pressure, the laminar flame speed for the NH₃/ air system is computed at 3 atm, Figure 2b. The modelling results are good for rich conditions, but somewhat higher than the experimental data under lean conditions. Experimental work is still required to obtain data at high pressures, which correspond to the AP combustion conditions in solid rocket motors. A sensitivity analysis is performed on this laminar flame case, for 1 atm. We define the sensitivity coefficient σ_k for reaction k via:

$$\sigma_k = \frac{\partial \ln(S_L)}{\partial \ln(\delta_k)} \quad (3)$$

Where S_L is the laminar flame speed and δ_k a perturbation applied to the pre-exponential factor of the reaction k . This coefficient is calculated for rich ($\phi = 1.8$) and lean ($\phi = 0.8$) conditions, and the reactions of the highest sensitivity are reported in Figure 3. It can be noted that for both considered equivalence ratios, the branching reaction R5 has the highest sensitivity.



The chemistry of N₂H₂ is also important in rich and lean environments. We notice that reaction R125 has adverse effects under lean and rich conditions.



Reactions involving NO_x have particular sensitivity when fuel is lacking, and little effect in rich mixtures.



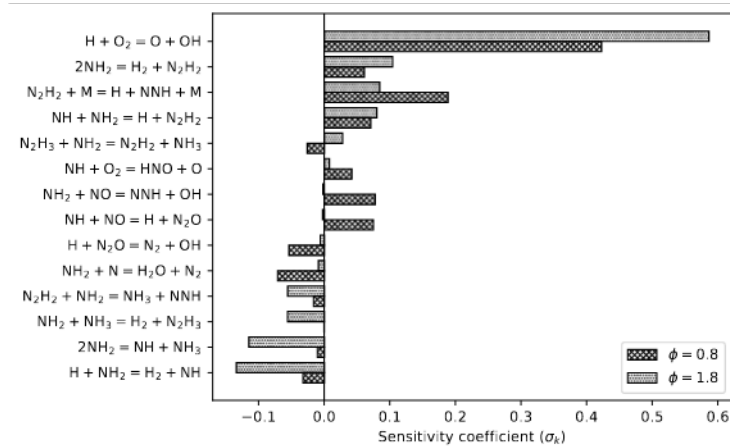


Fig. 3: Sensitivity coefficient for the laminar flame speed of the NH_3 / air system, at 1 atm and two equivalence ratios.

118 Finally, the reactions involving NH_x , such as R79, R87 and R99, are important in rich mixtures and less significant
 119 in lean environment.



120 More generally, we observe a notable variation of the reaction sensitivity with the equivalence ratio.

121 4.2. $\text{H}_2/\text{O}_2/\text{NO}_x$ Chemistry

122 Combustion of ammonium perchlorate leads to production of various NO_x species. It is therefore important
 123 to ensure the validity of the kinetics involving these species. The $\text{H}_2/\text{O}_2/\text{NO}_x$ sub-mechanism is validated on
 124 experiments in a jet-stirred reactor. The first test case, Figure 4, corresponds to a mixture of reactants H_2 (1%) /
 125 O_2 (1%) / N_2 doped with 220 ppm of NO . The pressure is 10 atm and the residence time is 1s.

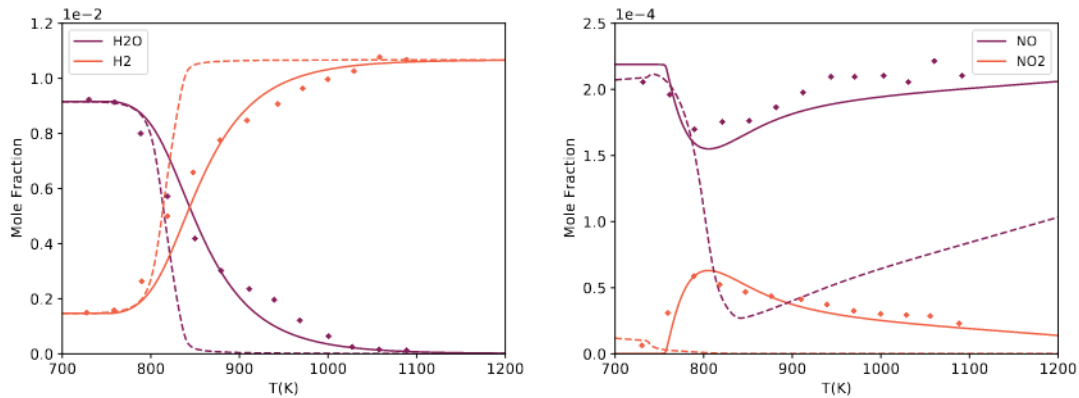


Fig. 4: Products in a jet-stirred reactor of the mixture H_2 (1%) / O_2 (1%) / N_2 with NO (220 ppm) at 10 atm, residence time 1 s, variable temperature. Symbols: experiment [27]. Solid lines: present model. Dashed lines: Gross model

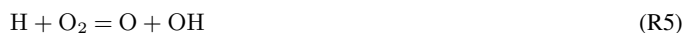
126 The Gross model [10] predicts correctly the crossover temperature of the H_2 and H_2O curves, around 825 K, but
 127 the results deviate rapidly from the experimental points as the temperature increases. The present model provides
 128 satisfactory results for the nitrogen-containing species. The crossover temperature is slightly over-predicted. The
 129 reaction is initiated by:



130 H_2 is then converted into H_2O via:



131 The rate of consumption of H_2 is therefore controlled by the concentration of OH in the gas. Three pathways
132 forming OH are identified:



133 At low temperature (700 K), these three reactions are almost inactive, prohibiting the conversion of H_2 to H_2O .
134 At 850 K, reaction R46 is particularly active: we observe conversion from NO to NO_2 and acceleration of the
135 hydrogen chemistry. At higher temperatures, reactions R5 and R46 are more active, reforming NO from NO_2 . In
136 the Gross model, reaction R46 is absent, which explains why the NO to NO_2 conversion process is not observed.
137 At 850 K, reactions R5 and R44 are very active: OH is produced in large quantities and the oxidation of H_2 is
138 strongly accelerated. The drop in the NO level is explained by its conversion via HNO into NO_2 , which is readily
139 transformed into OH via R44 to accelerate the H_2 oxidation.

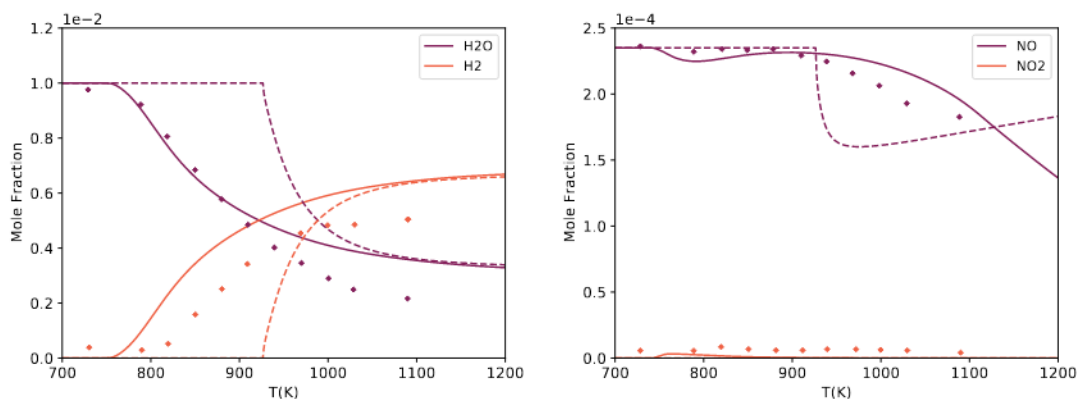


Fig. 5: Products in a jet-stirred reactor of the mixture H_2 (1%) / O_2 (0.333%) / N_2 doped with NO (235 ppm) at 1 atm, residence time 0.24 s, variable temperature. Symbols: experiment [27]. Solid lines: present model. Dashed lines: Gross model [10].

140 A similar case with a lower pressure (1 atm) and a higher equivalence ratio ($\Phi = 1.5$) is presented in Figure 5.
141 The profiles obtained with the present model for nitrogen-containing species are satisfactory. For H_2 and H_2O ,
142 the prediction is consistent with the results presented by Shrestha et al. [12]. The H_2 oxidation is again controlled
143 by the production of OH. At low temperature (800 K), OH is produced via R44 and R46. These two reactions
144 progress in the forward direction. Their balance is essential to ensure production of OH allowing the oxidation
145 H_2 at a correct rate, to avoid over-consuming or over-producing NO and NO_2 . The action of these two reactions
146 is less important at lower temperatures compared to the conversion phenomenon observed in Figure 4. At higher
147 temperatures, they contribute to the consumption of NO, explaining the decrease in the NO level observed around
148 1000K. As in the previous case, the Gross model presents a significant drop in the NO level which abruptly
149 accelerates the oxidation of H_2 . However, the onset of this process occurs at a much higher temperature than in
150 the experiment.

151 Another case, presented in Figure 6, is to study the effect of NO_2 as a doping species. A similar reactive mixture
152 as in the previous case is doped with 60 ppm of NO_2 at 10 atm. For both models the H_2 to H_2O conversion is
153 predicted satisfactorily, the NO_2 to NO conversion takes place via the reaction $\text{NO}_2 + \text{H} = \text{NO} + \text{OH}$. In the Gross
154 model, this reaction is too rapid, causing an overproduction of NO at low temperature; NO formed is then rapidly
155 converted into N_2 via the reaction $\text{NO} + \text{HNO} = \text{N}_2 + \text{HO}_2$ resulting in the low NO level at high temperature. This
156 last reaction is absent in the new model, providing a closer agreement with the experimentally measured NO level.

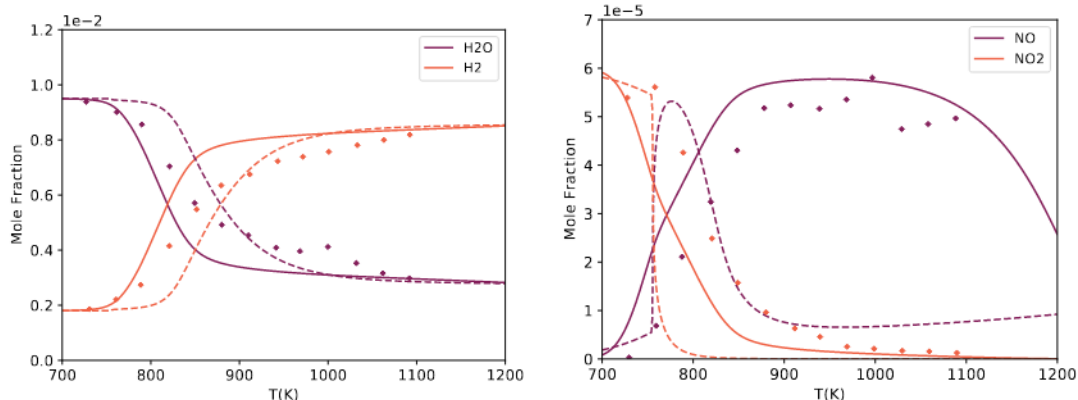


Fig. 6: Products in a jet-stirred reactor of the mixture H_2 (1%) / O_2 (0.333%) / N_2 doped with NO_2 (60 ppm) at 10 atm, 1 s residence time, variable temperature. Symbols: experiment [27]. Solid lines: present model. Dashed lines: Gross model [10].

157 The kinetic model is finally tested on a self-ignition case, for a H_2 (1%)/ O_2 (1%)/Ar mixture with 100 ppm of NO_2
 158 at various pressures (1.7, 13. and 33. atm), Figure 7. For the lowest pressure, the model predictions follow the
 159 linear trend, corresponding to the ignition regime controlled by the chain branching mechanism. However, the
 160 predicted transition due to chain termination at lower temperature or higher pressures is shifted to the left of the
 161 experimental points. The Gross model largely overpredicts the ignition delay time at all pressures.

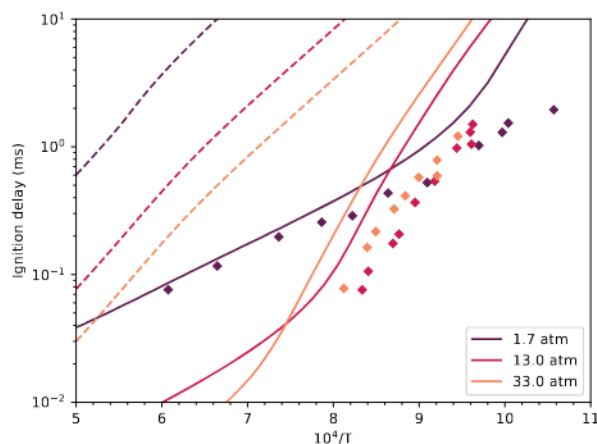


Fig. 7: Ignition delay time of a H_2 (1%)/ O_2 (1%)/Ar mixture with NO_2 (100 ppm) for various pressures (1.7, 13 and 33 atm), initial temperature 298 K. Symbols: experiment [28]. Solid lines: present model. Dashed lines: Gross model [10].

162 4.3. Cl_2 / H_2 Chemistry

163 The experimental and modeling results on the ignition delay time for different Cl_2 / H_2 / Ar mixtures are reported
 164 in Figure 8. The experimental points come from measurements made by Lifshitz and Schechner [29] in a shock
 165 tube over the temperature range 830 K to 1260 K. The cases considered are grouped in Table 3. The mole fractions
 166 shown represent the initial composition of the reactive mixture, P_1 is the initial pressure, and P_5 is the pressure
 167 after the reflected shock.

168 Cases A and B demonstrate the ability of the models to reproduce the effect of pressure on the ignition delay
 169 time for a stoichiometric mixture. Cases C, D, and E allow testing the effect of equivalence ratio at a constant
 170 pressure. Good agreement between the model curves and experimental points is observed for these cases at higher
 171 temperatures, but discrepancies increase at lower temperatures, particularly for cases C and E. In general, the
 172 present model produces systematically better predictions than the Gross model.

173 As reported by Pelucchi et al. [18], the ignition delay is mainly controlled by the R159 initiation reaction and the
 174 R163 branching reaction forming Cl and H radicals.

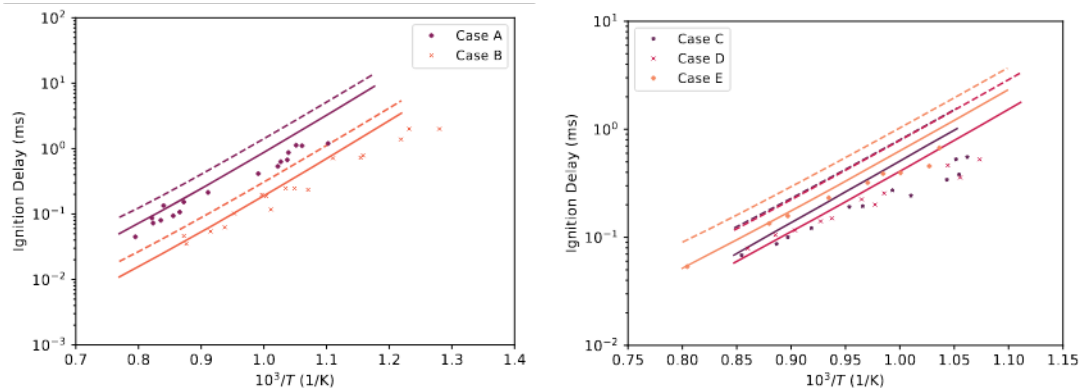
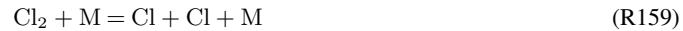


Fig. 8: Ignition delay time for $\text{Cl}_2/\text{H}_2/\text{Ar}$ mixtures. Cases are presented in Table 3. Symbols: experiment [29]. Solid lines: present model. Dashed lines: Gross model.

Table 3: Conditions for ignition modelling in $\text{Cl}_2/\text{H}_2/\text{Ar}$ mixtures and error norm of the model predictions.

Case	Cl_2 (%)	H_2 (%)	P_1 (atm)	P_5 (atm)	δ_{err} Gross	δ_{err} This work
A	10.4	10.4	0.066	1.0	$1.79 \cdot 10^0$	$9.83 \cdot 10^{-1}$
B	10.4	10.4	0.263	4.6	$1.49 \cdot 10^0$	$8.19 \cdot 10^{-1}$
C	19.8	10.0	0.066	1.3	$1.38 \cdot 10^0$	$7.74 \cdot 10^{-1}$
D	10.3	21.6	0.066	1.3	$1.42 \cdot 10^0$	$5.99 \cdot 10^{-1}$
E	11.0	11.0	0.066	1.3	$1.06 \cdot 10^0$	$4.71 \cdot 10^{-1}$



175 A more detailed analysis of the reaction kinetics could allow an improvement of the model predictions. The good
 176 performance observed at high temperature remains however sufficient for the combustion model of ammonium
 177 perchlorate.

178 The models are further validated on test cases of laminar flame speed for a $\text{Cl}_2 / \text{H}_2 / \text{N}_2$ mixture with different
 179 dilution levels, for which the results are shown in Figure 9. Deviations with respect to experimental data are
 180 presented in Table 4.

Table 4: Laminar flame speed for $\text{Cl}_2/\text{H}_2/\text{N}_2$ mixtures: error norm of the model predictions.

X_{N_2}	δ_{err} Gross	δ_{err} This work
0.5	$5.91 \cdot 10^{-1}$	$2.96 \cdot 10^{-1}$
0.55	$1.89 \cdot 10^0$	$1.62 \cdot 10^{-1}$
0.6	$3.78 \cdot 10^{-1}$	$1.38 \cdot 10^{-1}$

181 Good agreement is found between the experimental points and the predictions obtained with the present model.
 182 For the Gross model, the laminar flame speed is systematically underestimated. This defect increases for more
 183 concentrated mixtures. A sensitivity study is performed for a N_2 mole fraction of 0.5 to highlight the reactions
 184 controlling the Cl_2/H_2 chemistry, Figure 10. As for the ignition delay cases, the initiation reaction R159 and the
 185 branching reaction R163 have particular sensitivity in both rich and lean environments.

186 We notice that the sensitivity coefficient of the other reactions is much lower and varies significantly with the
 187 equivalence ratio. The reactions producing HCl other than the R163 pathway are:



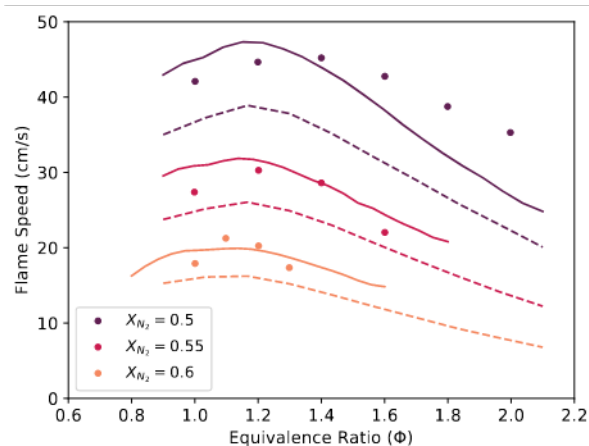


Fig. 9: Laminar flame speed for $\text{Cl}_2/\text{H}_2/\text{N}_2$ mixtures at 1 atm, 298 K, and different mole fractions of N_2 . Symbols: experiment [30]. Solid lines: present model. Dashed lines: Gross model [10].

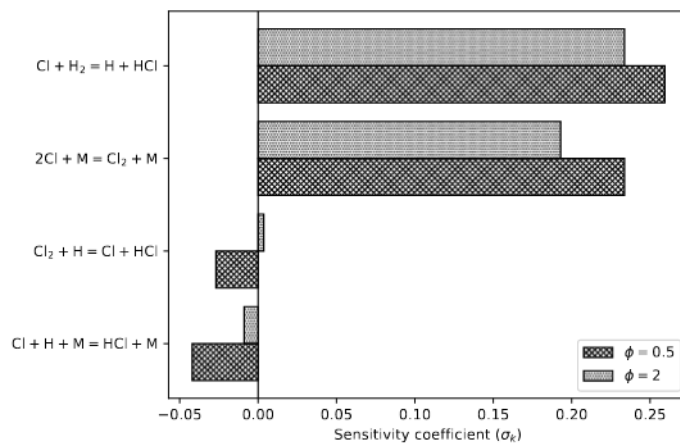


Fig. 10: Sensitivity coefficients of the laminar flame speed for $\text{Cl}_2/\text{H}_2/\text{N}_2$ mixtures at 1 atm, containing 50% of N_2 , in rich ($\phi = 2$) and lean ($\phi = 0.5$) environments.

188 These reactions have a relatively low sensitivity coefficient. They consume H radicals and have higher sensitivity
 189 at low equivalence ratio, when there are more Cl_2 and Cl atoms in the reacting mixture. Reaction R162 consumes
 190 H radicals but also produces Cl atoms needed for reaction R163, similar to the initiation reaction R159 ; its sensi-
 191 tivity coefficient is thus slightly positive in rich medium, when the mixture is at lack of Cl.

192 As a final comment on the sub-mechanism for chlorinated species, it is to be noted that one of the main products
 193 of AP decomposition is perchloric acid HClO_4 . The breakup of this molecule is hence an important step in the AP
 194 combustion process. The reactions modeling this step are taken from the historical mechanism of Ermolin et al.
 195 [17]. Kinetic studies of this particular molecule could greatly help the development of future combustion models
 196 for AP.

197
 198

5. Coupled Combustion Model

199 The new gas-phase kinetic mechanism is applied to the case of ammonium perchlorate combustion. Calculations
 200 are performed in a coupled approach with the condensed phase. A diagram of the simulation domain is presented
 201 in Figure 11, showing schematically the temperature profile and phase transformation. The gas and condensed
 202 phases are considered to be separated by a planar and infinitely thin interface, for which the coupling conditions
 203 are formulated. The combustion process is assumed to be one-dimensional and steady-state in the reference frame
 204 attached to the interface. This is a usual approach for modelling solid monopropellant combustion, see Rahman et
 205 al. [31].

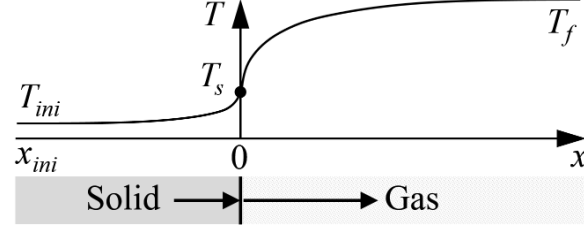


Fig. 11: Schematic representation of the temperature profile and phase transformation in a coupled combustion simulation

206 5.1. Governing Equations

207 5.1.1. Gas Phase

208 The governing equations for a reactive flow are formulated under the assumption of low Mach number. In the
 209 following expressions, index "g" designates bulk properties of the gas-phase and index "k" identifies the k-th
 210 chemical species.

211 The continuity equation is expressed as:

$$\frac{d}{dx} (\rho_g u) = 0 \quad (4)$$

212 Where ρ_g is the bulk density and u is the flow velocity. The gas density is determined as a function of the
 213 temperature and chemical species fractions for a given thermodynamic pressure. We then introduce the mass flux
 214 $m = \rho_g u$, constant in space. Under the adopted assumptions, the velocity is entirely defined by the continuity
 215 equation. The momentum equation allows obtaining the variation of the hydrodynamic pressure, which is not of
 216 interest to this problem. The equation for the mass fraction Y_k of chemical species is :

$$m \frac{dY_k}{dx} = - \frac{d}{dx} (\rho_g Y_k V_k) + \mathcal{M}_k \dot{\omega}_k \quad (5)$$

217 With \mathcal{M}_k the species molar mass, $\dot{\omega}_k$ its molar production rate and V_k its diffusion velocity. Finally, the energy
 218 equation is expressed as:

$$\begin{cases} m \frac{dh_g}{dx} = \frac{dQ_g}{dx} \\ Q_g = \lambda_g \frac{dT}{dx} - \rho_g \sum_{k=1}^{N_s} h_k Y_k V_k \end{cases} \quad (6)$$

219 Where T is the temperature, λ_g is the thermal conductivity, h_g and h_k are the mass-specific enthalpies.
 220 These equations are discretized by the finite volume method and solved by a Newton-Raphson algorithm. In order
 221 to facilitate the convergence, temporal terms are introduced and discretized using the backward Euler scheme. The
 222 inlet conditions are determined by the coupling equations with the condensed phase. The gradients of T and Y_k
 223 are assumed to be zero at the outlet boundary. The CHEMKIN library [32] is used for computing the reaction rates
 224 and thermodynamic properties in the gas phase. Molecular transport properties (thermal conductivity, diffusion
 225 coefficients) are evaluated employing the EGLib library [33, 34].

226 5.1.2. Condensed Phase

227 The condensed phase properties are designated by index "c". By analogy with the gas-phase, the mass flux in the
 228 condensed phase is $m = \rho_c u$, where ρ_c is the corresponding density.

229 The energy equation is:

$$\begin{cases} m \frac{dh_c}{dx} = \frac{dQ_c}{dx} \\ Q_c = \lambda_c \frac{dT}{dx} \end{cases} \quad (7)$$

230 Where h_c is the enthalpy, and λ_c is the thermal conductivity. This equation can be expressed as two ordinary
 231 differential equations:

$$\begin{cases} \frac{dT}{dx} = \nabla T \\ \frac{d}{dx} (\lambda_c \nabla T) = m c_c \nabla T \end{cases} \quad (8)$$

232 With c_c the mass-specific heat capacity of the condensed phase. These equations are integrated using the DASSL
 233 algorithm [35], from the initial conditions:

$$\begin{cases} T(x_{\text{ini}}) = T_{\text{ini}} \\ (\lambda_c \nabla T)_{\text{ini}} = m [h_c(T_{\text{ini}}) - h_c(T_0)] \end{cases} \quad (9)$$

234 With T_0 the initial temperature of the condensed phase. The thermophysical properties of the AP are defined as
 235 dependent on the temperature and its physical state. Table 5 presents the model parameters for the solid and liquid
 236 AP. The transition enthalpy from the solid to liquid state accounts for the transition enthalpy from the orthorhombic
 237 to cubic crystalline phase of AP.

Table 5: Thermophysical properties of AP

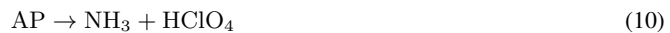
Property	Solid AP	Liquid AP	Ref
Density (kg/m ³)	1957	1756	[7]
Enthalpy at 298.15 K (J kg ⁻¹)	-2517423	-	[36]
Melting Temperature (K)	735	-	[11]
Transition Enthalpy (J kg ⁻¹)	-	338312	[36], [7]
Thermal Capacity (J kg ⁻¹ K ⁻¹)	584.35 + 1.7054T	1913	[37], [11]
Thermal Conductivity (W m ⁻¹ K ⁻¹)	0.642 - 3.849 · 10 ⁻⁴ T	0.416 - 1.569 · 10 ⁻⁴ T	[37], [11]

238 5.2. Interface Conditions

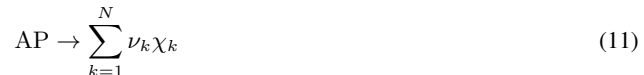
239 The interface between the condensed and gas phases is a particular zone to model, owing to the complexity of the
 240 physical phenomena involved. A chemically reactive foam is found in this zone. The mass and heat transfer is
 241 accompanied by decomposition reactions in the condensed phase. Few experimental results are available to model
 242 these mechanisms. The study of this interface is difficult due to its small thickness: Boggs et al. [38] reports a
 243 thickness of 1 to 5 μm , while Tanaka and Beckstead [7] estimate a thickness of less than 1 μm . It is proposed for
 244 the present modeling approach to consider this interface as an infinitely thin surface with appropriate conditions
 245 that are part of the present model. These conditions must ensure the transfer of mass, heat and species between
 246 the two phases while representing the chemical reactions taking place in the foam in a global sens.

247 5.2.1. Interface Chemistry

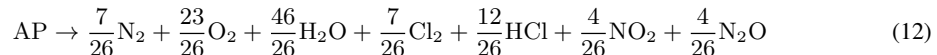
248 AP decomposition is represented by surface reactions. It is commonly assumed [10, 31, 39], that AP decomposes
 249 via two competing pathways. The first one is endothermic and results from direct sublimation of AP molecules
 250 via proton transfer and desorption:



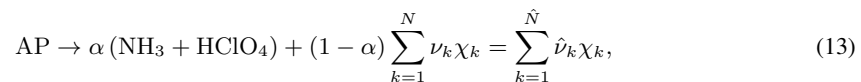
251 The second exothermic pathway, forming N chemical species and hereafter called “decomposition path”, is meant
 252 to model the remaining chemical reactions:



253 Where χ_k designates the k -th product species and ν_k its stoichiometric coefficient. Numerous variants have been
 254 proposed for this pathway by several authors [7, 10, 11]. These models produce unsatisfactory results when
 255 coupled with the gas-phase reaction mechanism presented above. A new formulation is therefore proposed to be
 256 used in the present model:



257 The relative importance of the two pathways is controlled by parameter α , such that the global reaction including
 258 both pathways can be written as:



259 where we introduce $\hat{\nu}_k$ the stoichiometric coefficient of species k . Since the sublimation and decomposition
 260 paths are respectively endothermic and exothermic, the α parameter has a first-order effect on the regression rate

261 predicted by the present model: the massflow rate increases as the value of α decreases. It is assumed in this
 262 study that α is independent of the ambient pressure and initial temperature of AP. It is fixed at a value of 0.65
 263 to reproduce the experimentally observed evolution of the regression rate as a function of the pressure. The regression
 264 mass flux m depends on the molar consumption rate of AP at the interface, $\hat{\omega}_{\text{AP}}$, which is related to the surface
 265 temperature via a pyrolysis law, Equation (14). Its parameters, specified in Table 6, are determined from a specific
 266 study detailed in Section 6.

$$m = -\mathcal{M}_{\text{AP}}\hat{\omega}_{\text{AP}} = A \exp\left(\frac{-T_a}{T_s}\right) \quad (14)$$

Table 6: Parameters for the AP pyrolysis law

Parameter	Value
\mathcal{M}_{AP} (kg mol ⁻¹)	0.11748
T_a (K)	7500
A (kg/m ² /s)	$3.0 \cdot 10^4$

267 5.2.2. Flux Conservation

268 We introduce the notation $[\cdot]$ such that:

$$[X] = X_g^I - X_c^I \quad (15)$$

269 Where X_c^I and X_g^I are quantities representing the boundary conditions for the condensed and gaseous phases.
 270 The interface is infinitely thin and is assumed to contain no source of mass or energy. The conservation of mass
 271 and energy fluxes across the interface leads to:

$$[m] = [\rho u] = 0 \quad (16)$$

$$[mh - Q] = 0 \quad (17)$$

272 The mass flux of species k in the gas phase is expressed at the interface as:

$$mY_k^I + (\rho_g Y_k V_k)^I = -\mathcal{M}_k \hat{\nu}_k \hat{\omega}_{\text{AP}} \quad (18)$$

273 We also impose the continuity of the temperature profile:

$$T_g^I = T_c^I = T_s \quad (19)$$

274 5.3. Solution Method for the Coupled Problem

275 Two one-dimensional physical domains are considered, for the condensed and gaseous phases. In order to
 276 ensure a correct coupling, a global iterative algorithm is employed to find the mass flow verifying the interface
 277 conditions. The residual defined by Equation must disappear through these iterations. At each global iteration, the
 278 solution in the condensed phase is obtained for the imposed mass flux by integrating Equations . The surface tem-
 279 perature is found from the pyrolysis law to verify the equability of the imposed mass flux and the surface regression
 280 rate defined by the pyrolysis law. The interface conditions for the gas phase are obtained via Equations and The
 281 mesh of the gas phase domain is automatically refined to limit the relative variation of the solution variables
 282 between each pair of adjacent cells and the relative variation of variable differences between three neighboring
 283 cells.

284 6. Pyrolysis Law

285 6.1. Parameters Choice

286 The overall combustion model can be broken down into three main founding blocks: the revised gas-phase kinetic
 287 model describing the reactions within the flame, the conformal condensed-phase reaction defining the gaseous
 288 species generated at the surface of the regressing propellant, and the pyrolysis law defining the dependance be-
 289 tween the surface temperature and regression rate. The pyrolysis law has a significant effect on the stability of
 290 the coupled flame / solid model. The combustion of ammonium perchlorate can be unstable under certain condi-
 291 tions, independently of external acoustic disturbances. This is the so-called intrinsic combustion instability of the
 292 propellant. These phenomena were studied by Denison and Baum [40], then by Zel'dovich and Novozhilov [13].

293 The two studies, following different reasoning, result in the same stability limit. According to the Zel'dovich-
 294 Novozhilov (ZN) theory, this limit is characterized by sensitivity parameters from the steady-state combustion of
 295 the propellant. We define these parameters at constant pressure:

$$k = (T_s - T_0) \left(\frac{\partial \ln m}{\partial T_0} \right)_P \quad (20)$$

$$r = \left(\frac{\partial T_s}{\partial T_0} \right)_P \quad (21)$$

296 Where k and r are the sensitivity coefficients of the mass flux and surface temperature to the initial propellant tem-
 297 perature T_0 . By introducing a small perturbation of the regression velocity and temperature field in the condensed
 298 phase and then linearizing the energy equation in the propellant, it is possible to obtain the stability condition:

$$r > r_L = \frac{(k - 1)^2}{k + 1} \quad (22)$$

299 We also define the temperature sensitivity coefficient of the propellant:

$$\sigma = \left(\frac{\partial \ln V_{reg}}{\partial T_0} \right)_P \quad (23)$$

300 When performing time-dependent simulations, it is important that the coupled combustion model is intrinsically
 301 stable. To this end, the pyrolysis law is designed making use of the ZN theory. Recalling the definition of the
 302 pyrolysis law, Equation (14), two constants need to be defined: the pre-exponential factor A , and the activation
 303 temperature T_a . It is to be noted that they are tunable parameters, and that multiple values can be found in the
 304 literature, see [7, 11]. The methodology described below is based on constraints to define the A and T_a parameters.
 305 A first constraint is to ensure stability of the coupled combustion model. Employing the ZN stability condition,
 306 Equation (22), the coupled combustion model will be stable up to pressure P if:

$$r = r_L \quad (24)$$

307 The values of r and r_L implicitly depend on the pressure and selected set (A, T_a) . Performing coupled sim-
 308 ulations for various values of (A, T_a) , the sets verifying Equation (24) are found. These sets define curves
 309 $A = A_{min}(T_a, P)$, which are shown in Figure 12 for various pressures. A first constraint on the selection of
 310 (A, T_a) is then the stability condition at pressure P :

$$A > A_{min}(T_a, P) \quad (25)$$

311 For a selected activation temperature and a given pressure, if we choose $A > A_{min}(T_a, P)$ the model is stable
 312 at this pressure, inequality (25) providing the ZN stability condition $r > r_L$. With $A < A_{min}(T_a, P)$, the time-
 313 dependent solution would display an oscillatory instability. This can be explained by the existence of a minimal
 314 mass-flow rate, below which not enough energy is fed back from the flame to the burning propellant such as to
 315 maintain its regression. One can note that $A_{min}(T_a, P)$ increases with pressure: the stability constraint (25)
 316 becomes more stringent as pressure grows up.

317 When selecting the parameters (A, T_a) of the pyrolysis law, the stability condition $A > A_{min}(T_a, P)$ is not
 318 restrictive enough. Indeed, applying the stability constraint as described above, the activation temperature T_a is
 319 still a free parameter. To add more constraints, one can use Equation (14), which explicitly defines a relation
 320 between the surface temperature and regression rate:

$$T_s = \frac{T_a}{\ln \left(\frac{A}{\rho_c V_{reg}} \right)} \quad (26)$$

321 The parameters (A, T_a) should be chosen so that Equation (26) correlates with experimental data. The discrepancy
 322 between the analytical relation (26) and available experimental data points [2–4] can be assessed via the following
 323 L_2 error norm:

$$\delta_{err}(A, T_a) = \left[\frac{1}{N} \sum_{i=1}^N \left(T_s^i - \frac{T_a}{\ln \left(\frac{A}{\rho_c V_{reg}^i} \right)} \right)^2 \right]^{\frac{1}{2}} \quad (27)$$

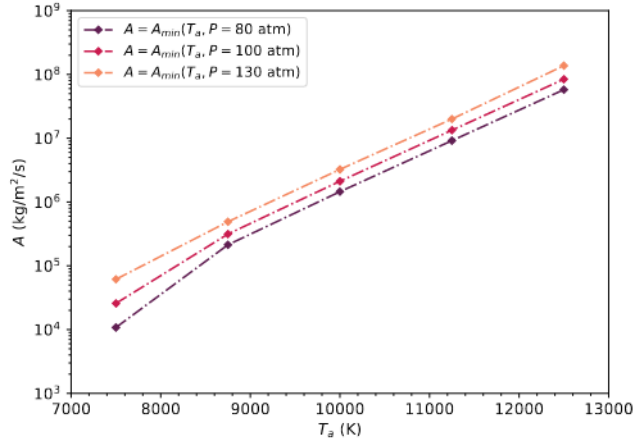


Fig. 12: Evolution $A = A_{min}(T_a, P)$ versus the activation temperature, for different pressures (80, 100 and 130 atm). Initial temperature of the solid AP: 298 K.

324 Where N is the number of experimental data points, and the i -th data point is (V_{reg}^i, T_s^i) .
 325 The second constraint on the selection of (A, T_a) is then that this set of values is to minimize $\delta_{err}(A, T_a)$. For a
 326 selected activation temperature, we define $A^*(T_a)$ minimizing this deviation, as:

$$A^*(T_a) = \arg \left(\min_A \delta_{err}(A, T_a) \right) \quad (28)$$

327 The evolution of $\delta_{err}(A, T_a)$ versus A is presented in Figure 13 for various activation temperatures. With these
 328 curves, the values of $A^*(T_a)$ are determined and marked by points. The curves $T_s = f(V_{reg})$ obtained from
 329 the analytical relations $T_s(A^*(T_a), T_a)$, defined by Equation (26), are traced in Figure 14. Because of the large
 330 scatter of the experimental data points, the choice of T_a is not evident.

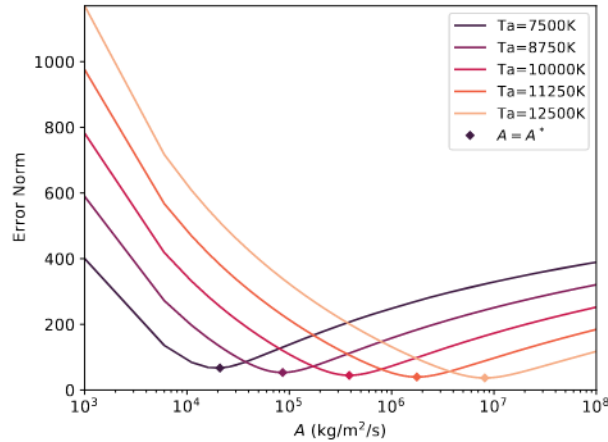


Fig. 13: Evolution of $\delta_{err}(A, T_a)$ with A for various activation temperatures, Equation (27).

331 In order to select the values of A and T_a , the curves $A = A_{min}(T_a, P)$ are plotted for various pressures, together
 332 with the curve $A = A^*(T_a)$, Figure 15. The selected set (A, T_a) must ensure the ZN stability of the coupled
 333 combustion model up to a high pressure. It must also provide results on $T_s(V_{reg})$ in agreement with the experi-
 334 mental data, *i.e.* A must be chosen close to $A^*(T_a)$. It is seen from Figure 15 that it is impossible to ensure the
 335 model stability up to 130 atm without using values of A which would deviate too much from $A^*(T_a)$. A good
 336 compromise is found selecting $A = 3 \cdot 10^4 \text{ kg/m}^2/\text{s}$ and $T_a = 7500 \text{ K}$. These values ensure the stability of the
 337 coupled combustion model up to at least 100 atm, and providing a small value of $\delta_{err}(A, T_a)$.

338 6.2. Effect on Macroscopic Parameters

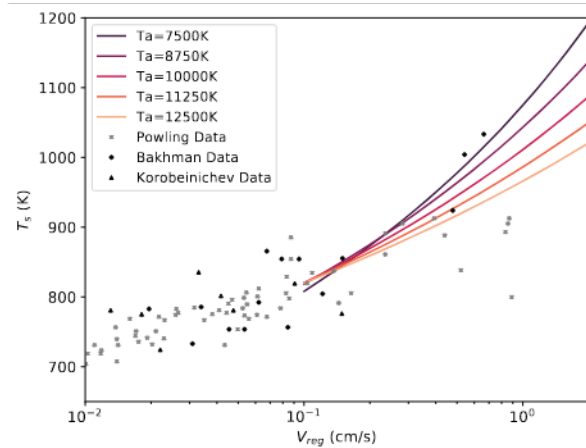


Fig. 14: Dependency between AP surface temperature and regression rate for various T_a and $A = A^*(T_a)$, Equation (26). Symbols: experiments [2–4]. Lines: computed relations.

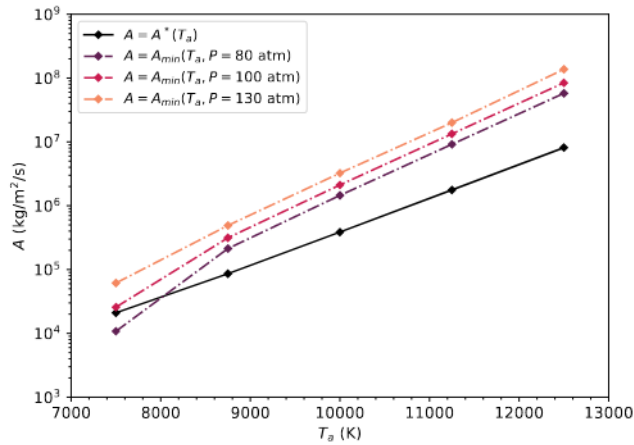


Fig. 15: Comparison of the curves $A = A_{min}(T_a, P)$ for different pressures (80, 100 and 130 atm), with the curve $A = A^*(T_a)$.

339 It is also of interest to study the effect of the pyrolysis law parameters on some macroscopic characteristics of the
 340 combustion: the regression rate V_{reg} , and surface temperature T_s . The modelling results are presented in Figure
 341 16 for a pressure of 100 atm.

342 For a given activation temperature, the regression rate first increases as a function of the pre-exponential factor,
 343 as the heat feedback to the condensed phase increases with growing mass-flow rate; on the other hand, the sur-
 344 face temperature is steadily decreasing, following the direct relationship between A , T_a and V_{reg} provided by the
 345 pyrolysis law (26). At the maximum of regression rate, the pre-exponential factor reaches a critical value, above
 346 which the regression rate decreases slowly. At this point, the surface temperature becomes too low and chemical
 347 reactions are slowed down near the AP surface, hence reducing the heat feedback to the condensed phase. When
 348 this progressive phenomenon becomes apparent, the surface temperature is below 900 K for the considered pres-
 349 sure. The value of the regression rate maximum does not depend on the activation temperature, and is mainly
 350 controlled by the value of parameter α determining the overall thermal effect of the condensed phase decompo-
 351 sition. Depending on the activation temperature, the point $A = A_{min}(T_a, P = 100 \text{ atm})$ on the curve $V_{reg}(A)$
 352 changes its location with respect to the maximum: it is on the left branch for $T_a = 7500 \text{ K}$, at the maximum for
 353 $T_a = 8750 \text{ K}$, and on the right branch for greater values of T_a .

354 The effect of the pyrolysis law parameters on the sensitivity coefficient σ is shown in Figure 17, for a pres-
 355 sure of 100 atm. The temperature sensitivity appears to be an increasing function of the pre-exponential factor
 356 A . The slope of the curve $\sigma(A)$ decreases with the activation temperature rise. Note that the value of σ for
 357 $A = A_{min}(T_a, P = 100 \text{ atm})$ depends on T_a within the lower part of the studied range and becomes stable at

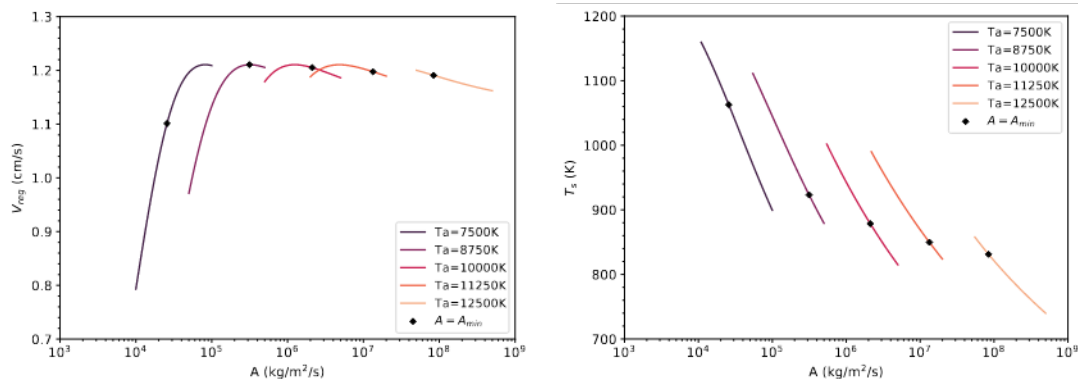


Fig. 16: Calculated regression rate (left) and surface temperature (right) versus pre-exponential factor for different activation temperatures. Ambient pressure 100 atm. Initial condensed-phase temperature 298 K.

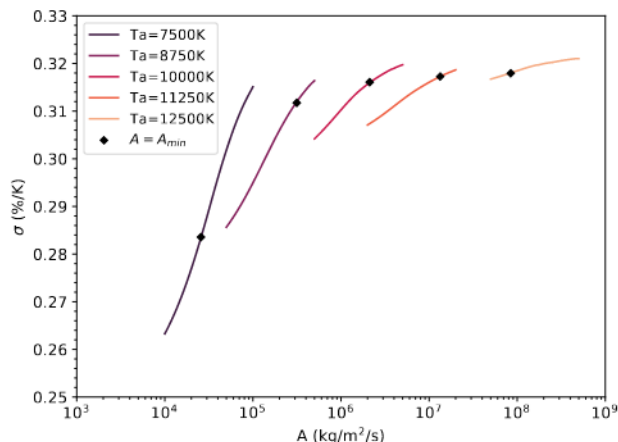


Fig. 17: Calculated sensitivity coefficient versus pre-exponential factor for different activation temperatures. Ambient pressure 100 atm. Initial condensed-phase temperature 298 K.

358 $T_a \geq 1000\text{ K}$.

359

360

7. AP Combustion Results

361

7.1. Ermolin's Flame

362

The coupled approach described above is first applied to the case of the low-pressure AP flame studied by Ermolin et al. [5] and Tereshchenko et al. [6]. The species mole fraction profiles, obtained with the present model and with the Gross reference model, are compared with the experimental data for the main AP flame products and nitrogen-containing species, Figure 18.

364

365

The present model provides results in agreement with the experimental data. On the other hand, the Gross model appears to suffer from deficiencies, mainly for nitrogen-containing species. The N_2 level is over-predicted above the surface, and an important rise is observed around $x = 10^{-2}\text{ cm}$, whereas the experimental data shows a slight increase in N_2 . The present model produces a significant amount of NO, whereas the Gross model predicts a low NO level within the flame. Hence, with this latter model, nitrogen-containing species are converted at an excessive rate to the final product N_2 , without forming enough NO as an intermediate species.

371

372

The temperature profile computed with the present model is presented in Figure 19, and compared against the experimental data from Tereshchenko et al. [6]. The results obtained with the Gross model [10] and two more models from the literature (Smyth et al. [11], Meynet et al. [9]) are presented as well. Most modeling results are in good agreement with this experimental temperature profile, with the exception of the Gross model which significantly overestimates the flame temperature. Smyth and Meynet also used this temperature profile as a validation case in their modeling studies. The compared profiles differ mainly in the predicted surface temperature and the downstream behaviour. In the Meynet model, the surface temperature is fixed at 825 K resulting in a significantly

373

374

375

376

377

378

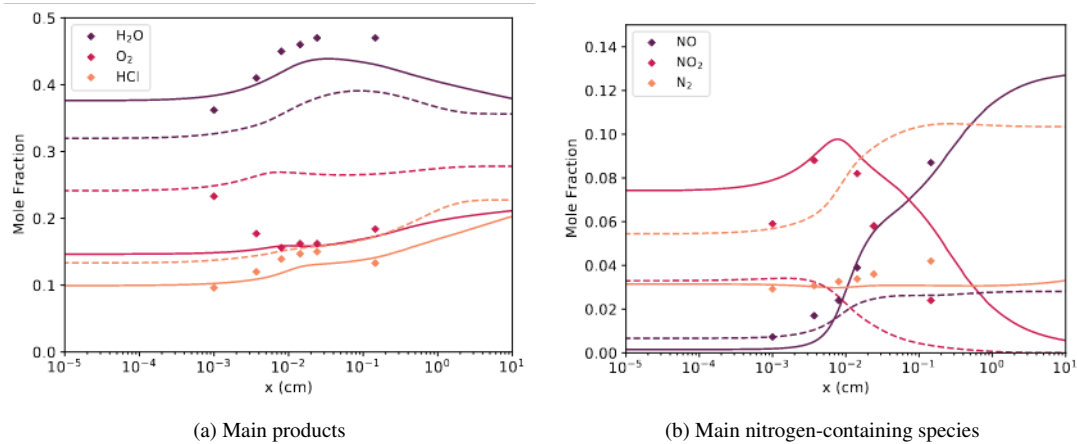


Fig. 18: Species profiles for the AP flame at 0.6 atm and initial temperature 533 K. Symbols: experiment [5]. Solid lines: present model. Dashed lines: Gross model [10].

379 higher temperature near the surface. The Smyth model profile is particularly distinguished by a second marked
 380 rise of temperature around $x = 1$ cm.

381 It is to be noted that this flame is the only AP combustion test case in the literature with available experimental
 382 profiles. Since the original publication from Ermolin et al. [5] in 1981, no significant progress has been made in
 383 the experimental characterisation of the AP flames. With a single available test case, a large variety of combustion
 384 models emerged over the years, each predicting more or less correctly the Ermolin flame, but with sometimes very
 385 different underlying physics. Experimental work on this matter, for instance at higher pressure, would be a great
 386 benefit for the solid propellant community.

387

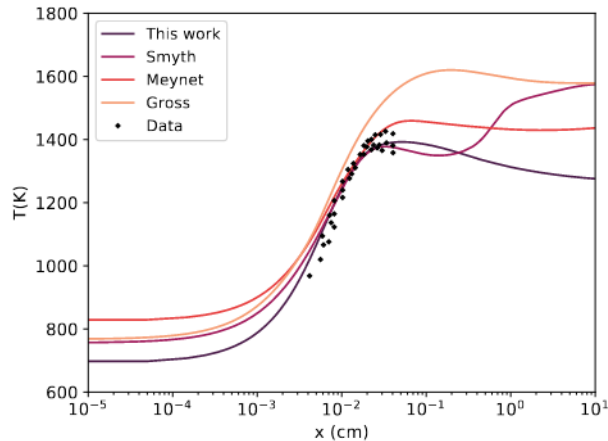


Fig. 19: Temperature profiles in the AP flame at 0.6 atm and initial temperature 533 K. Symbols: experiment [6]. Lines: model prediction.

388 The NO and N₂ profiles predicted with the different models are shown in Figure 20. The observed rapid conversion
 389 of NO into N₂ is due to the irreversible reaction $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$ in the Smyth model. The second temperature
 390 rise obtained with the Smyth model is caused by the energy released by this specific reaction. This reaction
 391 was introduced in order to decrease the NO level past the flame front, judged by Smyth et al. to be too far
 392 from the thermochemical equilibrium. Such an irreversible and non-elemental reaction appears to be artificial and
 393 destabilizes the equilibrium of the NO_x chemistry. The proposed model, whose NO_x chemistry has been previously
 394 validated on experimental cases, predicts a significant level of NO and reproduces the experimental points of
 395 [5]. These results suggest that NO may indeed be an important end product for the AP flame: thermochemical
 396 equilibrium could be reached far downstream of the flame front.

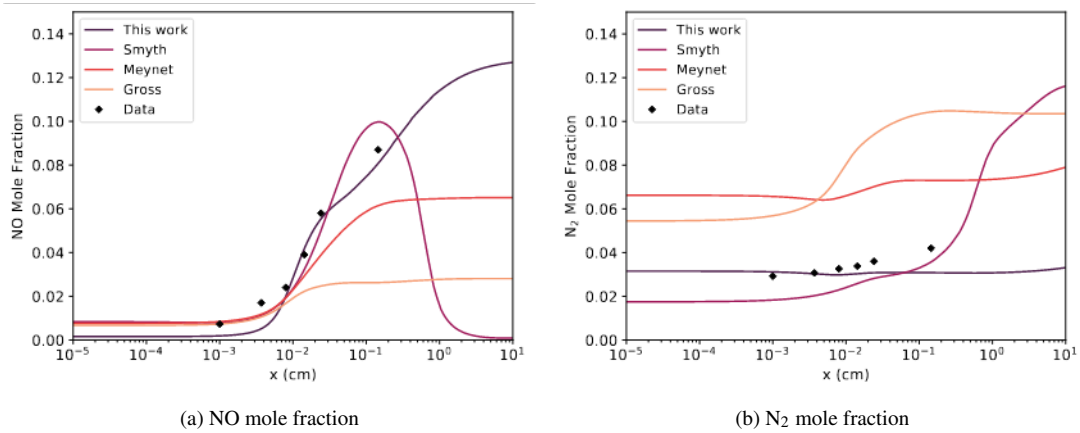


Fig. 20: Profiles of NO and N₂ in the AP flame at 0.6 atm and initial temperature 533 K. Symbols: experiment [5]. Lines: model prediction.

397 7.2. Macroscopic Combustion Parameters

398 The validity of the coupled model is further verified by computing macroscopic characteristics of AP combustion.
 399 The evolution of AP regression rate versus pressure is presented in Figure 21, or the four combustion models
 400 compared in the previous test case. Satisfying agreement is obtained between computed results and experimental
 401 data points, for all models. Indeed, they were all adjusted to fit these points. For a given gas-phase kinetic model,
 402 the condensed-phase decomposition model can be adapted to ensure sufficient heat production at the AP surface.
 403 The ratio α between the exothermic and endothermic decomposition pathways, Equation (13), has a first order
 404 effect on the regression rate and can be tuned to this end. With suitable formulation of the AP decomposition
 405 products and pyrolysis law, it is possible to obtain correct evolution of the regression rate with pressure for pure
 406 AP using quite different gas-phase mechanisms. On the other hand, gas-phase kinetics becomes critical when simulating
 407 the combustion of composite propellants: decomposition and combustion products of pure AP react with
 408 species produced by the pyrolysis of the binder. A diffusion flame formed near the AP/binder interface provides
 409 intense surface heating due to the additional heat release, thereby increasing the local regression rate. Therefore,
 410 a correct representation of the gas-phase kinetics within the AP flame is a necessary first step to accurately model
 411 the combustion of AP-based composite propellants.

412 The curves obtained with the different models can be approximated by a Vieille law of the form:

$$V_{\text{reg}} = aP^n \quad (29)$$

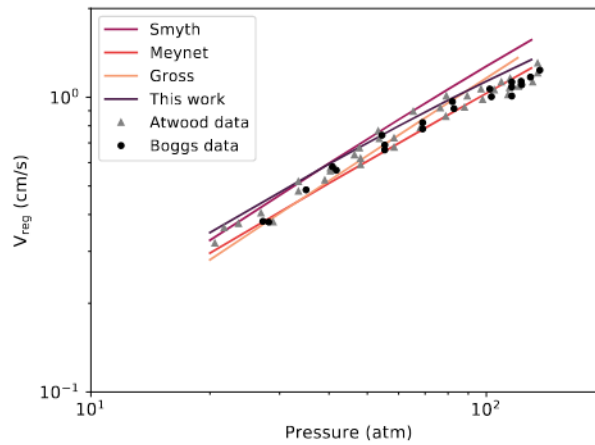


Fig. 21: AP regression rate as a function of pressure. Initial temperature 298 K. Symbols: experiments [1, 38]. Lines: model predictions.

413 Where V_{reg} is the regression speed and P is the ambient pressure. We note that n is independent of pressure for the

414 models of Gross, Meynet and Smyth. In the case of the present model, n decreases with pressure. This behaviour
 415 is consistent with the experimental results: the AP regression rate curve exhibits a decrease in its slope at high
 416 pressure. Thus, while the Smyth model slightly overestimates the measured regression rate at pressures higher
 417 than 80 atm, the present model observes the experimental trend other the whole pressure range. This behaviour of
 418 the present model is a consequence of the choice of the pyrolysis law. Looking at Figure 16, the design point for
 419 the current model is located in the steep region of the curve $V_{\text{reg}}(A)$ for $P = 100$ atm. The regression rate tends
 420 to move farther from the maximum value achievable with increasing pressure, explaining the variability of n .
 421 The evolution of the AP surface temperature with the regression rate is shown in Figure 22. The Meynet model
 422 assumes the surface temperature to be independent of the regression rate and equal to the melting temperature of
 423 AP (825 K in this model). This assumption appears to be too simplifying in view of the higher surface temperatures
 424 experimentally observed. The curve produced by the present model is above the Smyth model curve for high
 425 regression rates, but still indicates acceptable temperatures considering the large scatter in the experimental data
 426 in this range of regression rate.

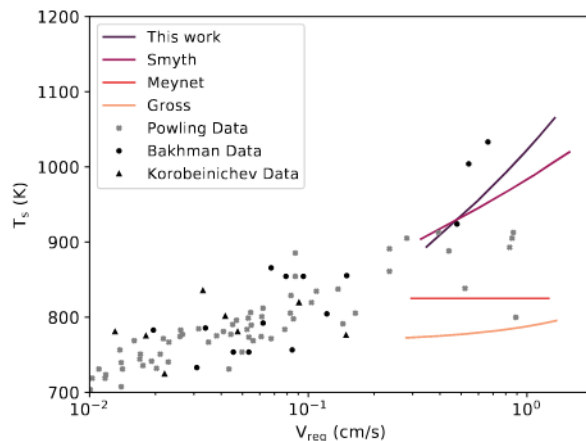


Fig. 22: AP surface temperature as a function of regression rate. Initial temperature 298 K. Symbols: experiments [2–4]. Lines: model prediction.

427 The parameters k and r have been calculated according to the ZN theory, Equation (20). The model of Meynet
 428 is not included in this analysis, as it assumes a fixed surface temperature. The Gross model isn't considered as well,
 429 as it uses separate correlations for the surface temperature and regression rate with respect to the surface heat flux,
 430 which is not a good approach for unsteady simulations. Both models are stable at low pressure and approach the
 431 stability limit as the pressure increases. In order to characterize more precisely the stability limit of the two models,
 432 the evolution with pressure of the stability margin $r - r_L$ is plotted in Figure 23. The combustion becomes unstable
 433 following an oscillatory regime below the zero level. The Smyth model becomes unstable around 87.5 atm, while
 434 the present model is stable up to 105 atm, as predicted when designing the pyrolysis law. This increased stability
 435 range is of practical interest, allowing unsteady calculations to be performed over a broader range of pressure.
 436 The trends of the temperature sensitivity $\sigma(P)$ for the different models considered are plotted in Figure 24. They
 437 are compared to the experimental data of Atwood et al. [1]. It is observed that the experimental trend is not
 438 captured by the models, as they predict a nearly constant temperature sensitivity over the studied pressure range.
 439 The present model predictions are at the upper boundary of the experimental data points scatter.

440
441

8. Conclusion

442 Using recent research by Shrestha et al. [12] and Pelucchi et al. [18], a revised gas-phase mechanism for AP
 443 combustion has been elaborated. This new mechanism produces satisfactory results for simple reactive systems,
 444 allowing validation of its main sub-mechanisms. The test cases also revealed deficiencies in the reference model
 445 from Gross et al. [10]: this mechanism was never validated on fundamental data, yet managed to reproduce the
 446 available macroscopic experimental data on AP combustion. This work highlights the importance of the valida-
 447 tion process when assembling a complex gas-phase mechanism: as testing macroscopic combustion characteristics
 448 (e.g. regression rate) cannot reveal possible deficiencies in the temperature and species profiles. But when try-
 449 ing to simulate the combustion of composite propellants, interactions between species from different ingredients
 450 would be very sensitive to the local conditions in the flame. A conformal condensed-phase decomposition model
 451 has been designed for the revised kinetic mechanism, including the gaseous product composition and an adapted

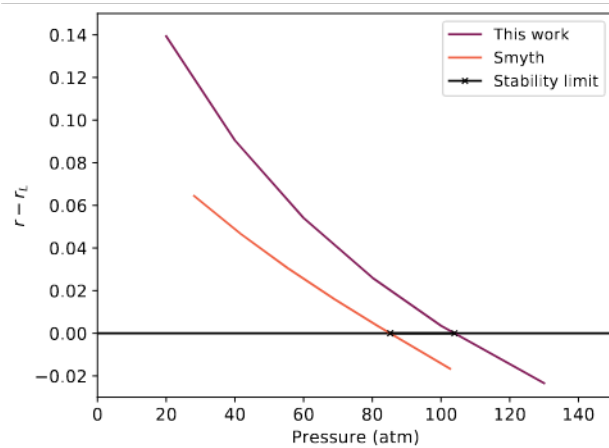


Fig. 23: Stability limit according to the ZN theory for different models.

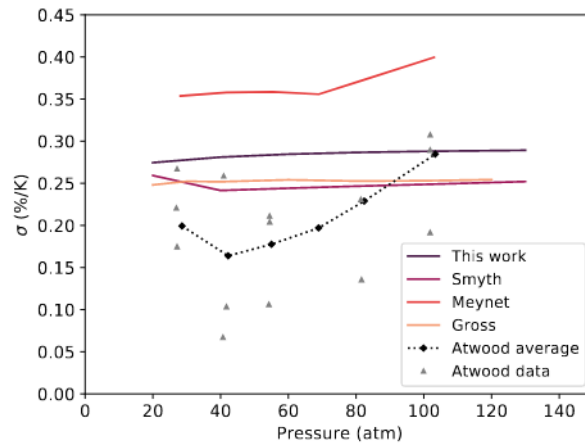


Fig. 24: Temperature sensitivity as a function of pressure. Symbols: experiment [1]. Lines: models [9–11].

452 pyrolysis law. The pyrolysis law parameters have been chosen ensuring combustion models stability up to 100
 453 atm. The resulting coupled model has been validated on the case of the low-pressure AP flame studied by Ermolin
 454 et al. [5] and Tereshenko et al. [6]. The profiles of the main species molar fraction and the temperature profile
 455 obtained are in good agreement with the available experimental data. The macroscopic characteristics of AP com-
 456 bustion (surface temperature, regression rate) were evaluated at different pressures. The regression rate shows a
 457 pressure dependence of the form aP^n with n decreasing with pressure. This result is consistent with experimental
 458 trend and represents a specificity of the new model compared to other reference models. A Zel'dovich-Novozhilov
 459 stability study was performed at variable pressure. The model is intrinsically stable up to 105 atm, allowing for
 460 unsteady simulation to be performed over a wide range of pressure. The evolution of the temperature sensitivity
 461 coefficient agrees with the experimental data.

462

463

9. Acknowledgments

464

The authors would like to thank Direction Générale de l'Armement and ONERA for funding and supporting
 465 the present work.

466

References

467

[1] A. I. Atwood, T. L. Boggs, P. O. Curran, T. P. Parr, D. M. Hanson-Parr, C. F. Price, J. Wiknich, Burning rate of solid
 468 propellant ingredients, part 1: Pressure and initial temperature effects, *J. Propul. Power* 15 (1999) 740–747.

469

[2] N. N. Bakhman, Y. S. Kichin, S. M. Kolyasov, A. E. Fogelzang, Investigation of the thermal structure of the burning zone
 470 in condensed mixtures by fine thermocouples, *Combust. Flame* 26 (1976) 235–247.

- 471 [3] J. Powling, Experiments relating to the combustion of ammonium perchlorate-based propellants, *Symp. (Int.) Combust.*
472 11 (1967) 447–456.
- 473 [4] O. P. Korobeinichev, A. A. Zenin, A. G. Tereshchenko, V. M. Puchkov, Investigation of the structure of a combustion wave
474 of mixed systems based on apc, pmma, and a catalyst using mass-spectrometric and thermocouple methods, *Combust.,*
475 *Explo. Shock.* 13 (1977) 273–279.
- 476 [5] N. E. Ermolin, V. M. Fomin, O. P. Korobeinichev, A. G. Tereshchenko, Measurement of the concentration profiles of
477 reacting components and temperature of an ammonium perchlorate flame, *Combust., Explo. Shock.* 18 (1982) 36–38.
- 478 [6] A. G. Tereshchenko, O. P. Korobeinichev, Correctness of mass-spectrometric probe measurements when investigating the
479 flame structure of condensed systems, *Combust., Explo. Shock.* 18 (1983) 645–650.
- 480 [7] M. Tanaka, M. Beckstead, A three-phase combustion model of ammonium perchlorate, 32nd Joint Propulsion Conference
481 and Exhibit, 1996, p. 2888.
- 482 [8] Q. Jing, M. Beckstead, M. Jeppson, Influence of AP solid-phase decomposition on temperature profile and sensitivity, 36th
483 AIAA Aerospace Sciences Meeting and Exhibit, 1998, p. 448.
- 484 [9] N. Meynet, Simulation numérique de la combustion d'un propergol solide, Ph.D. thesis, Université Paris VI (2005).
- 485 [10] M. L. Gross, Two-dimensional modeling of AP/HTPB utilizing a vorticity formulation and one-dimensional modeling of
486 AP and ADN, Ph.D. thesis, Brigham Young University (2007).
- 487 [11] D. A. Smyth, Modeling solid propellant ignition events, Ph.D. thesis, Brigham Young University (2011).
- 488 [12] K. P. Shrestha, L. Seidel, T. Zeuch, F. Mauss, Detailed kinetic mechanism for the oxidation of ammonia including the
489 formation and reduction of nitrogen oxides, *Energ. Fuel.* 32 (2018) 10202–10217.
- 490 [13] B. V. Novozhilov, Theory of nonsteady burning and combustion stability of solid propellants by the Zeldovich-Novozhilov
491 method, in: *Nonsteady Burning and Combustion Stability of Solid Propellants*, American Institute of Aeronautics and
492 Astronautics, 1992, pp. 601–641.
- 493 [14] K. P. Shrestha, C. Lhuillier, A. A. Barbosa, P. Brequigny, F. Contino, C. Mounaim-Rousselle, L. Seidel, F. Mauss, An
494 experimental and modeling study of ammonia with enriched oxygen content and ammonia/hydrogen laminar flame speed
495 at elevated pressure and temperature, *Symp. (Int.) Combust.* 38 (2021) 2163–2174.
- 496 [15] J. B. Baker, R. K. Rahman, M. Pierro, J. Higgs, J. Urso, C. Kinney, S. Vasu, Experimental ignition delay time measurements
497 and chemical kinetics modeling of hydrogen/ammonia/natural gas fuels, *J. Eng. Gas. Turb. Power* 145 (2023) 041002.
- 498 [16] M. D. Smooke, R. A. Yetter, T. P. Parr, D. M. Hanson-Parr, M. A. Tanoff, M. B. Colket, R. J. Hall, Computational
499 and experimental study of ammonium perchlorate/ethylene counterflow diffusion flames, *Proc. Combust. Inst.* 28 (2000)
500 2013–2020.
- 501 [17] N. E. Ermolin, Model for chemical reaction kinetics in perchloric acid-ammonia flames, *Combust., Explo. Shock.* 31
502 (1995) 555–565.
- 503 [18] M. Pelucchi, A. Frassoldati, T. Faravelli, B. Ruscic, P. Glarborg, High-temperature chemistry of HCl and Cl₂, *Combust.*
504 *Flame* 162 (2015) 2693–2704.
- 505 [19] D. G. Goodwin, R. L. Speth, H. K. Moffat, B. W. Weber, Cantera: An object-oriented software toolkit for chemical kinetics,
506 thermodynamics, and transport processes (2021). doi:<https://doi.org/10.5281/zenodo.4527812>.
- 507 [20] O. Mathieu, E. L. Petersen, Experimental and modeling study on the high-temperature oxidation of ammonia and related
508 nox chemistry, *Combust. Flame* 162 (2015) 554–570.
- 509 [21] A. Hayakawa, T. Goto, R. Mimoto, Y. Arakawa, T. Kudo, H. Kobayashi, Laminar burning velocity and markstein length of
510 ammonia/air premixed flames at various pressures, *Fuel.* 159 (2015) 98–106.
- 511 [22] V. F. Zakaznov, L. A. Kursheva, Z. I. Fedina, Determination of normal flame velocity and critical diameter of flame
512 extinction in ammonia-air mixture, *Combust., Explo. Shock.* 14 (1978) 710–713.
- 513 [23] U. J. Pfahl, M. C. Ross, J. E. Shepherd, K. O. Pasamehmetoglu, C. Unal, Flammability limits, ignition energy, and flame
514 speeds in H₂-CH₄-NH₃-N₂O-O₂-N₂ mixtures, *Combust. Flame* 123 (2000) 140–158.
- 515 [24] P. D. Ronney, Effect of chemistry and transport properties on near-limit flames at microgravity, *Combust. Sci. Technol.* 59
516 (1988) 123–141.
- 517 [25] T. Jabbour, D. F. Clodic, Burning velocity and refrigerant flammability classification, *ASHRAE Tran.* 110 (2004) 522.
- 518 [26] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, Burning velocity measurements of nitrogen-containing
519 compounds, *J. Hazard. Mater.* 155 (2008) 144–152.
- 520 [27] G. Dayma, P. Dagaut, Effects of air contamination on the combustion of hydrogen-effect of NO and NO₂ addition on
521 hydrogen ignition and oxidation kinetics, *Combust. Sci. Technol.* 178 (2006) 1999–2024.
- 522 [28] O. Mathieu, A. Levacque, E. Petersen, Effects of no₂ addition on hydrogen ignition behind reflected shock waves, *Symp.*
523 *(Int.) Combust.* 34 (2013) 633–640.
- 524 [29] A. Lifshitz, P. Schechner, The mechanism of the H₂+ Cl₂ reaction: ignition behind reflected shocks, *Int. J. Chem. Kinet.*
525 7 (1975) 125–142.
- 526 [30] J. C. Lylegian, H. Y. Sun, C. K. Law, Laminar flame speeds and kinetic modeling of hydrogen/chlorine combustion,
527 *Combust. Flame* 143 (2005) 199–210.
- 528 [31] S. Rahman, V. Giovangigli, V. Borie, Pressure and initial temperature sensitivity coefficient calculations in ammonium
529 perchlorate flames, *J. Propul. Power* 27 (2011) 1054–1063.
- 530 [32] R. J. Kee, F. M. Rupley, E. Meeks, J. A. Miller, Chemkin-II: A FORTRAN chemical kinetics package for the analysis of
531 gas-phase chemical and plasma kinetics, Tech. Rep. SAND-89-8009, Sandia National Laboratories, Livermore, CA, USA
532 (5 1989).
- 533 [33] A. Ern, V. Giovangigli, *Multicomponent Transport Algorithms*, Vol. 24, Springer Science & Business Media, 1994.
- 534 [34] A. Ern, V. Giovangigli, Fast and Accurate Multicomponent Transport Property Evaluation, *J. Comput. Phys.* 120 (1995)
535 105–116.
- 536 [35] L. R. Petzold, Description of DASSL: a differential/algebraic system solver, Tech. Rep. SAND-82-8637, Sandia National
537 Laboratories, Livermore, CA, USA (1982).

- 538 [36] M. W. Chase, NIST-JANAF Thermochemical Tables, 4th Edition, American Institute of Physics, 1998.
- 539 [37] D. M. Hanson-Parr, T. P. Parr, Thermal properties measurements of solid rocket propellant oxidizers and binder materials
540 as a function of temperature, *J. Energ. Mater.* 17 (1999) 1–48.
- 541 [38] T. L. Boggs, Deflagration rate, surface structure, and subsurface profile of self-deflagrating single crystals of ammonium
542 perchlorate, *AIAA J.* 8 (1970) 867–873.
- 543 [39] C. Guirao, F. A. Williams, A model of ammonium perchlorate deflagration between 20 and 100 atm, *AIAA J.* 9 (1971)
544 1345–1356.
- 545 [40] M. R. Denison, E. Baum, A simplified model of unstable burning in solid propellants, *ARSJ-Am Rocket Soc J.* 31 (1961)
546 1112–1122.