



**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-04148974v1>**

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<sup>a,†</sup>, Dmitry Davidenko<sup>a</sup>, Laurent Catoire<sup>b</sup>

<sup>a</sup> DMPE, ONERA, Université Paris Saclay, 91120 Palaiseau, France

<sup>b</sup> 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  $\text{NO}_x$  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 ( $\text{NH}_3\text{HClO}_4$ ) decomposes in the condensed phase via different pathways, the most impor-  
39 tant of them forming  $\text{NH}_3$  and  $\text{HClO}_4$ . The presence of  $\text{NH}_3$  among the main decomposition products requires an  
40 appropriate kinetic model for  $\text{NH}_3$ , its subsequent radicals, and  $\text{NO}_x$ . 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  $\text{NH}_3$  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/Cl<sub>2</sub> 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 NH<sub>3</sub>/O<sub>2</sub> chemistry is first  
 64 validated via laminar flame speed and ignition delay calculations. The H<sub>2</sub>/O<sub>2</sub>/NO<sub>x</sub> chemistry is tested on experi-  
 65 ments in a jet-stirred reactor and a shock tube. The correct treatment of the Cl<sub>2</sub>/H<sub>2</sub> 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  $\mu_y$  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. NH<sub>3</sub> / O<sub>2</sub> Chemistry

81 Ammonia (NH<sub>3</sub>) is one of the main decomposition products of ammonium perchlorate. In order to validate the  
 82 oxidation sub-mechanism of NH<sub>3</sub>, different experiments are reproduced with the present model. The ignition delay  
 83 time for a highly diluted NH<sub>3</sub>/O<sub>2</sub> 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 NH<sub>3</sub>/O<sub>2</sub> mixtures: error norm of the model predictions.

| $\phi$ | P (atm) | $\delta_{err}$       |
|--------|---------|----------------------|
| 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 NH<sub>3</sub> and O<sub>2</sub>, nor dissociation reaction for these species. The ignition is initiated in the present mechanism via  
 89 reactions R92 and R97:



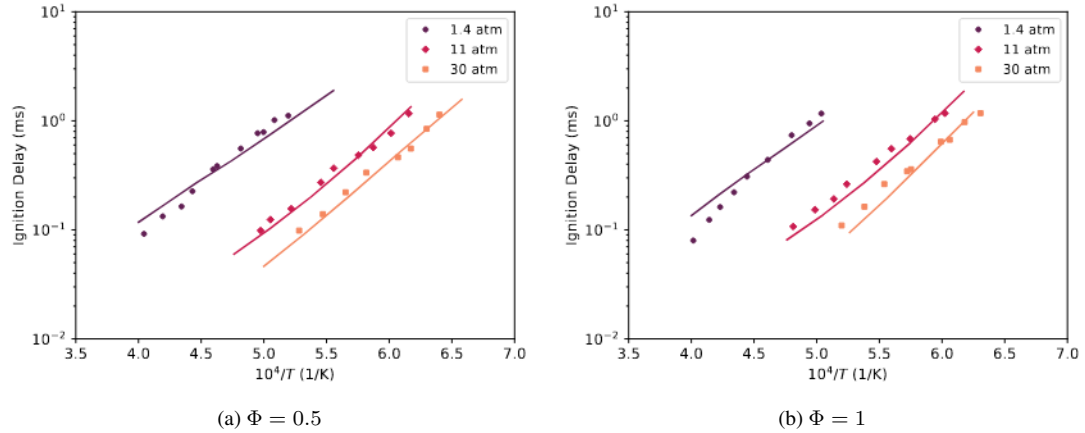


Fig. 1: Ignition delay time of  $\text{NH}_3/\text{O}_2$  mixtures for various pressure (1.4, 11 and 30 atm) and equivalence ratio ( $\phi = 0.5$  and 1), initial temperature 298 K. Symbols: experiment [20]. Lines: model predictions.

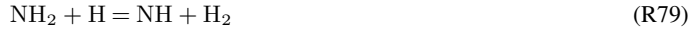
90 Reaction R92 is particularly important. It produces hydrogen atoms, which participate in the formation of the OH  
 91 and O radicals via the following reaction:



92 The ammonia  $\text{NH}_3$  is then transformed into  $\text{NH}_2$  by reactions with O, H and OH radicals:



93 Reactions R93 and R94 consume the majority of  $\text{NH}_3$ .  $\text{NH}_2$  is then converted via two paths, forming NH and  
 94  $\text{N}_2\text{H}_2$  respectively:



95 The final product  $\text{N}_2$  is mainly formed from  $\text{N}_2\text{H}_2$  via the intermediary NNH:



96 Several hydrogen-abstraction reactions involving  $\text{NH}_x$  produce  $\text{H}_2$ , which is finally converted into  $\text{H}_2\text{O}$  via:



97 The predicted laminar flame speeds for the  $\text{NH}_3$  / 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 NH<sub>3</sub>/ air mixtures at 1 atm: error norm of the model predictions.

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

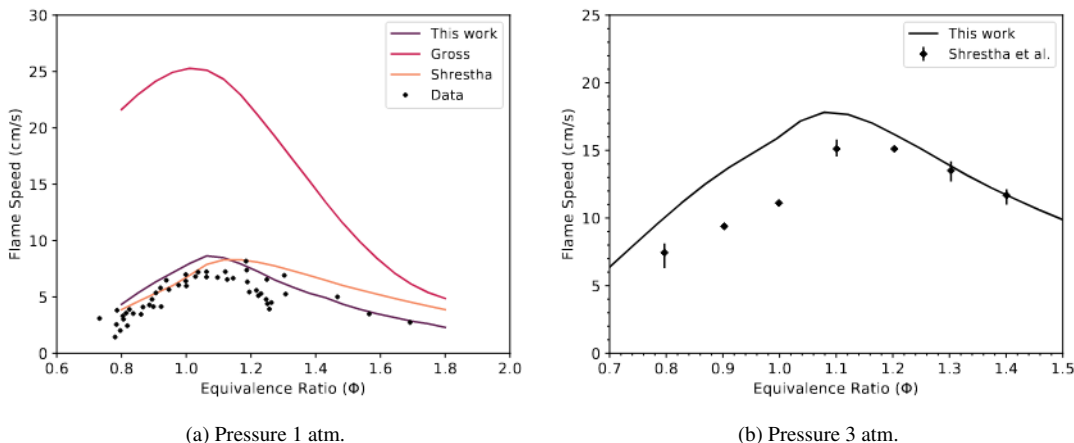


Fig. 2: Laminar flame speed versus equivalence ratio for NH<sub>3</sub>/air mixtures at 298 K and for two pressures. Symbols: experiments. (a) [21–26], (b) [14]. Lines: Model predictions.

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 NH<sub>3</sub>/ 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  $\sigma_k$  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  $\delta_k$  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 N<sub>2</sub>H<sub>2</sub> is also important in rich and lean environments. We notice that reaction R125 has adverse effects under lean and rich conditions.



Reactions involving NO<sub>x</sub> have particular sensitivity when fuel is lacking, and little effect in rich mixtures.



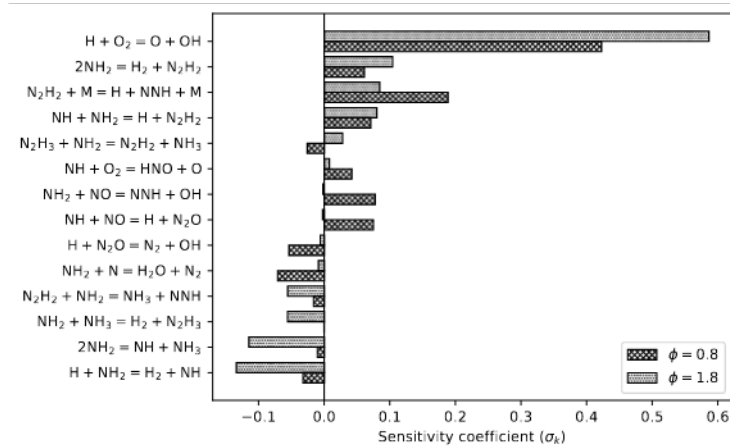


Fig. 3: Sensitivity coefficient for the laminar flame speed of the  $\text{NH}_3$  / air system, at 1 atm and two equivalence ratios.

118 Finally, the reactions involving  $\text{NH}_x$ , 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  $\text{NO}_x$  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  $\text{H}_2$  (1%) /  
 125  $\text{O}_2$  (1%) /  $\text{N}_2$  doped with 220 ppm of  $\text{NO}$ . The pressure is 10 atm and the residence time is 1s.

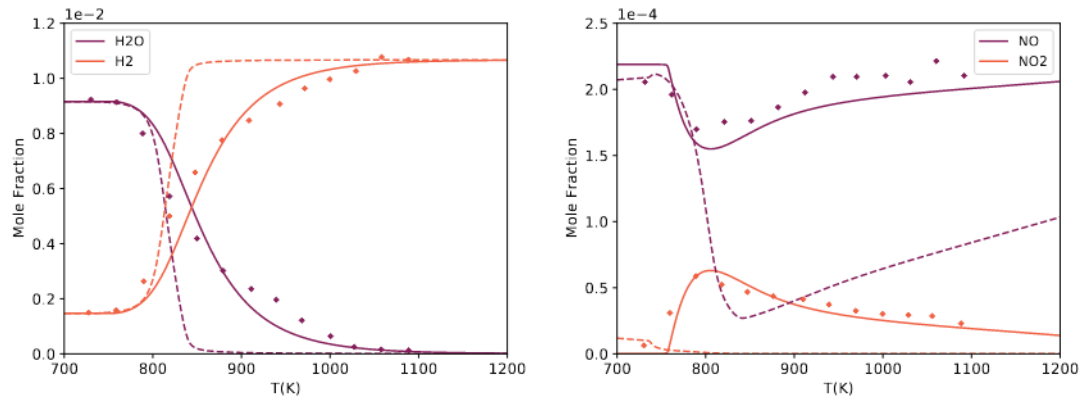


Fig. 4: Products in a jet-stirred reactor of the mixture  $\text{H}_2$  (1%) /  $\text{O}_2$  (1%) /  $\text{N}_2$  with  $\text{NO}$  (220 ppm) at 10 atm, residence time 1 s, variable temperature. Symbols: experiment [27]. Solid lines: present model. Dashed lines: Gross model

126 The Gross model [10] predicts correctly the crossover temperature of the  $\text{H}_2$  and  $\text{H}_2\text{O}$  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  $\text{H}_2$  is then converted into  $\text{H}_2\text{O}$  via:



131 The rate of consumption of  $\text{H}_2$  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  $\text{H}_2$  to  $\text{H}_2\text{O}$ .  
134 At 850 K, reaction R46 is particularly active: we observe conversion from NO to  $\text{NO}_2$  and acceleration of the  
135 hydrogen chemistry. At higher temperatures, reactions R5 and R46 are more active, reforming NO from  $\text{NO}_2$ . In  
136 the Gross model, reaction R46 is absent, which explains why the NO to  $\text{NO}_2$  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  $\text{H}_2$  is  
138 strongly accelerated. The drop in the NO level is explained by its conversion via HNO into  $\text{NO}_2$ , which is readily  
139 transformed into OH via R44 to accelerate the  $\text{H}_2$  oxidation.

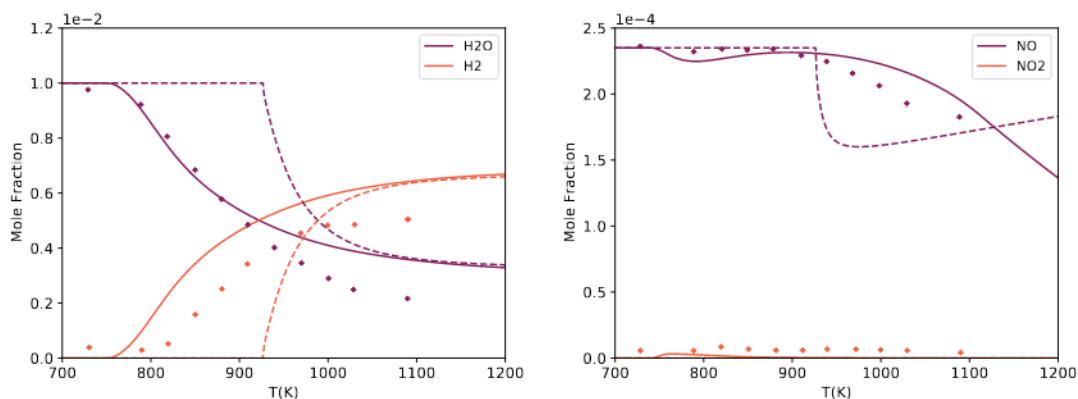


Fig. 5: Products in a jet-stirred reactor of the mixture  $\text{H}_2$  (1%) /  $\text{O}_2$  (0.333%) /  $\text{N}_2$  doped with NO (235 ppm) at 1 atm, residence time 0.24 s, variable temperature. Symbols: experiment [27]. Solid lines: present model. Dashed lines: Gross model [10].

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  $\text{H}_2$  and  $\text{H}_2\text{O}$ ,  
142 the prediction is consistent with the results presented by Shrestha et al. [12]. The  $\text{H}_2$  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  $\text{H}_2$  at a correct rate, to avoid over-consuming or over-producing NO and  $\text{NO}_2$ . 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  $\text{H}_2$ . 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  $\text{NO}_2$  as a doping species. A similar reactive mixture  
152 as in the previous case is doped with 60 ppm of  $\text{NO}_2$  at 10 atm. For both models the  $\text{H}_2$  to  $\text{H}_2\text{O}$  conversion is  
153 predicted satisfactorily, the  $\text{NO}_2$  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  $\text{N}_2$  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.



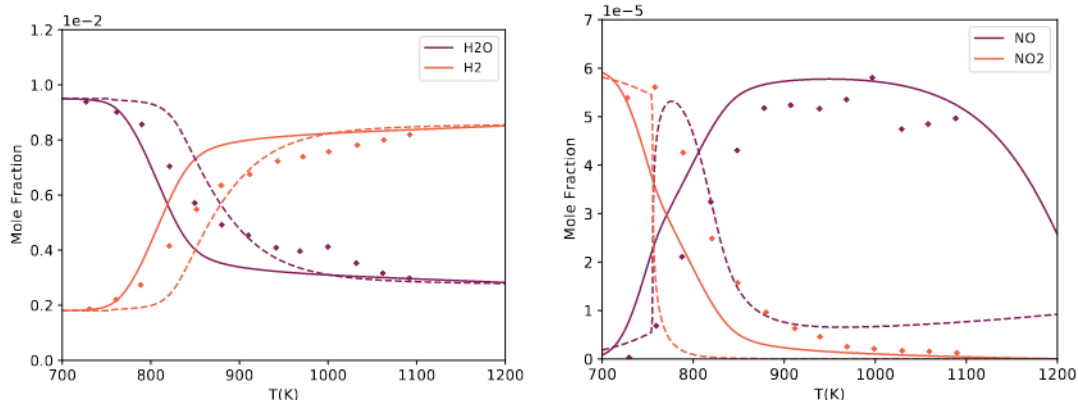


Fig. 6: Products in a jet-stirred reactor of the mixture  $\text{H}_2$  (1%) /  $\text{O}_2$  (0.333%) /  $\text{N}_2$  doped with  $\text{NO}_2$  (60 ppm) at 10 atm, 1 s residence time, variable temperature. Symbols: experiment [27]. Solid lines: present model. Dashed lines: Gross model [10].

157 The kinetic model is finally tested on a self-ignition case, for a  $\text{H}_2$  (1%)/ $\text{O}_2$ (1%)/Ar mixture with 100 ppm of  $\text{NO}_2$   
 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.

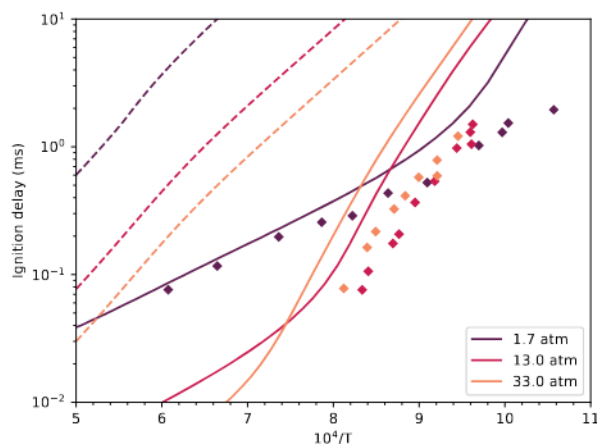


Fig. 7: Ignition delay time of a  $\text{H}_2$  (1%)/ $\text{O}_2$ (1%)/Ar mixture with  $\text{NO}_2$  (100 ppm) for various pressures (1.7, 13 and 33 atm), initial temperature 298 K. Symbols: experiment [28]. Solid lines: present model. Dashed lines: Gross model [10].

#### 162 4.3. $\text{Cl}_2$ / $\text{H}_2$ Chemistry

163 The experimental and modeling results on the ignition delay time for different  $\text{Cl}_2$  /  $\text{H}_2$  / 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.

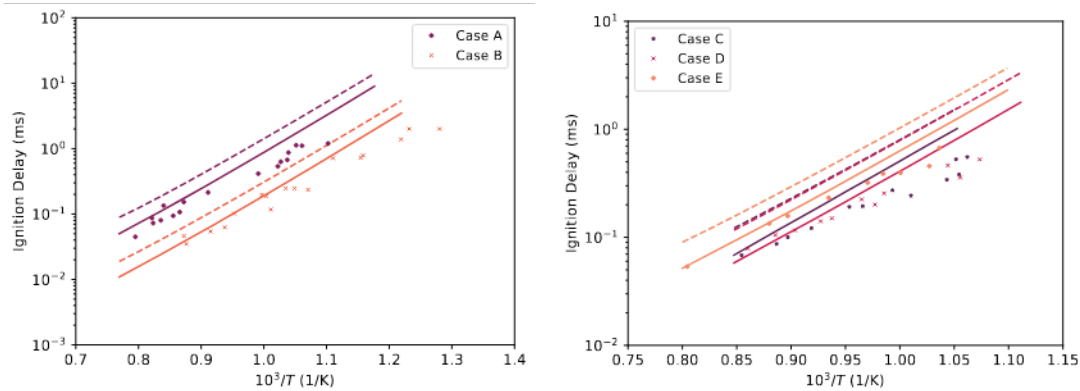


Fig. 8: Ignition delay time for  $\text{Cl}_2/\text{H}_2/\text{Ar}$  mixtures. Cases are presented in Table 3. Symbols: experiment [29]. Solid lines: present model. Dashed lines: Gross model.

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

| Case | $\text{Cl}_2$ (%) | $\text{H}_2$ (%) | $P_1$ (atm) | $P_5$ (atm) | $\delta_{err}$ Gross | $\delta_{err}$ 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.

| $X_{\text{N}_2}$ | $\delta_{err}$ Gross | $\delta_{err}$ 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  $\text{N}_2$  mole fraction of 0.5 to highlight the reactions  
 184 controlling the  $\text{Cl}_2/\text{H}_2$  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:



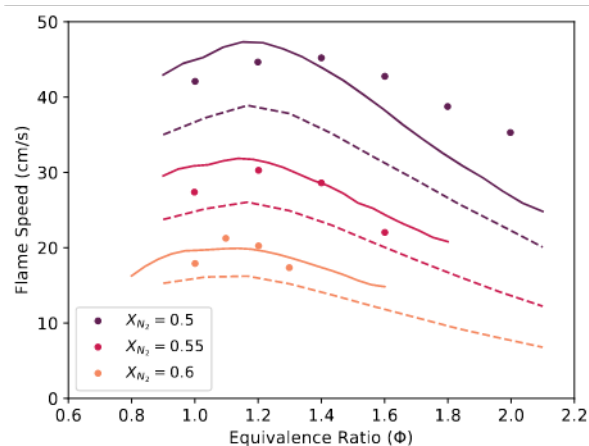


Fig. 9: Laminar flame speed for  $\text{Cl}_2/\text{H}_2/\text{N}_2$  mixtures at 1 atm, 298 K, and different mole fractions of  $\text{N}_2$ . Symbols: experiment [30]. Solid lines: present model. Dashed lines: Gross model [10].

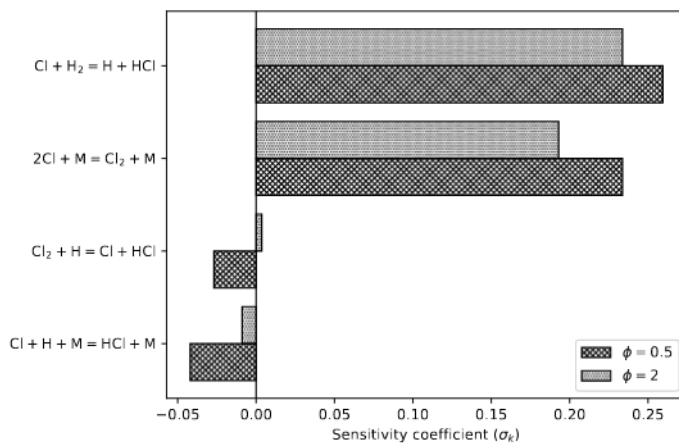


Fig. 10: Sensitivity coefficients of the laminar flame speed for  $\text{Cl}_2/\text{H}_2/\text{N}_2$  mixtures at 1 atm, containing 50% of  $\text{N}_2$ , in rich ( $\phi = 2$ ) and lean ( $\phi = 0.5$ ) environments.

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  $\text{Cl}_2$  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  $\text{HClO}_4$ . 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].

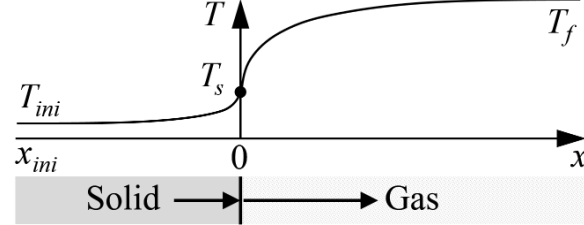


Fig. 11: Schematic representation of the temperature profile and phase transformation in a coupled combustion simulation

## 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  $\rho_g$  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,  $\lambda_g$  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  $\rho_c$  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  $\lambda_c$  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 <sup>3</sup> )                              | 1957                               | 1756                               | [7]        |
| Enthalpy at 298.15 K (J kg <sup>-1</sup> )                | -2517423                           | -                                  | [36]       |
| Melting Temperature (K)                                   | 735                                | -                                  | [11]       |
| Transition Enthalpy (J kg <sup>-1</sup> )                 | -                                  | 338312                             | [36], [7]  |
| Thermal Capacity (J kg <sup>-1</sup> K <sup>-1</sup> )    | 584.35 + 1.7054T                   | 1913                               | [37], [11] |
| Thermal Conductivity (W m <sup>-1</sup> K <sup>-1</sup> ) | 0.642 - 3.849 · 10 <sup>-4</sup> T | 0.416 - 1.569 · 10 <sup>-4</sup> 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  $\mu\text{m}$ , while Tanaka and Beckstead [7] estimate a thickness of less than 1  $\mu\text{m}$ . 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

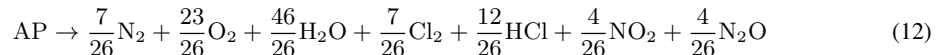
248 AP decomposition is represented by surface reactions. It is commonly assumed [10, 31, 39], that AP decomposes  
 249 via two competing pathways. The first one is endothermic and results from direct sublimation of AP molecules  
 250 via proton transfer and desorption:



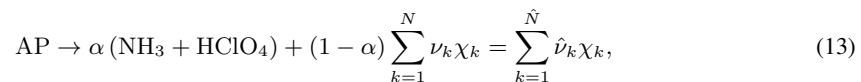
251 The second exothermic pathway, forming  $N$  chemical species and hereafter called “decomposition path”, is meant  
 252 to model the remaining chemical reactions:



253 Where  $\chi_k$  designates the  $k$ -th product species and  $\nu_k$  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  $\alpha$ , 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  $\alpha$  parameter has a first-order effect on the regression rate

261 predicted by the present model: the massflow rate increases as the value of  $\alpha$  decreases. It is assumed in this  
 262 study that  $\alpha$  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            |
|---|------------------|
| $\mathcal{M}_{\text{AP}}$ (kg mol <sup>-1</sup> ) | 0.11748          |
| $T_a$ (K)   | 7500             |
| $A$ (kg/m <sup>2</sup> /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:

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

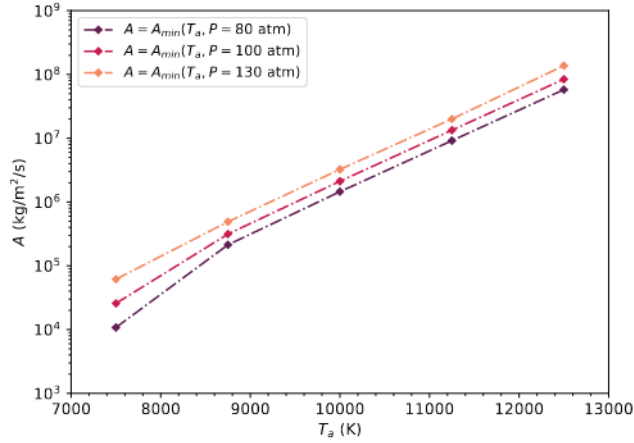


Fig. 12: Evolution  $A = A_{min}(T_a, P)$  versus the activation temperature, for different pressures (80, 100 and 130 atm). Initial temperature of the solid AP: 298 K.

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.

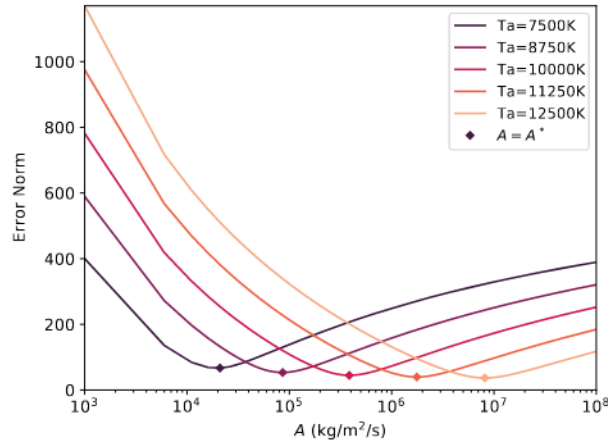


Fig. 13: Evolution of  $\delta_{err}(A, T_a)$  with  $A$  for various activation temperatures, Equation (27).

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



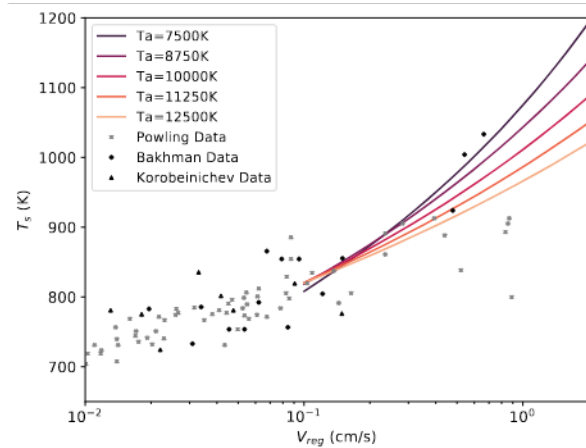


Fig. 14: Dependency between AP surface temperature and regression rate for various  $T_a$  and  $A = A^*(T_a)$ , Equation (26). Symbols: experiments [2–4]. Lines: computed relations.

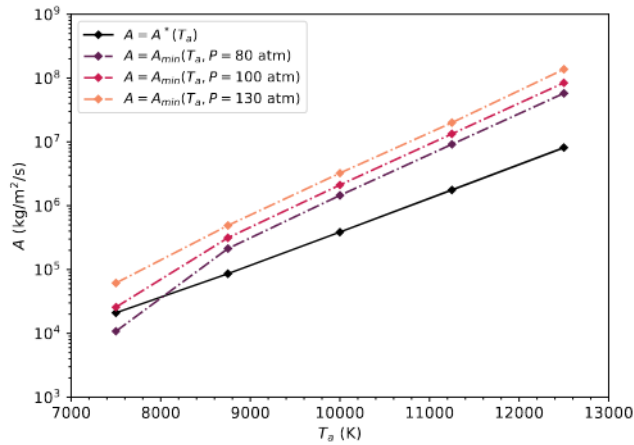


Fig. 15: Comparison of the curves  $A = A_{min}(T_a, P)$  for different pressures (80, 100 and 130 atm), with the curve  $A = A^*(T_a)$ .

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  $\alpha$  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  $\sigma$  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  $\sigma$  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

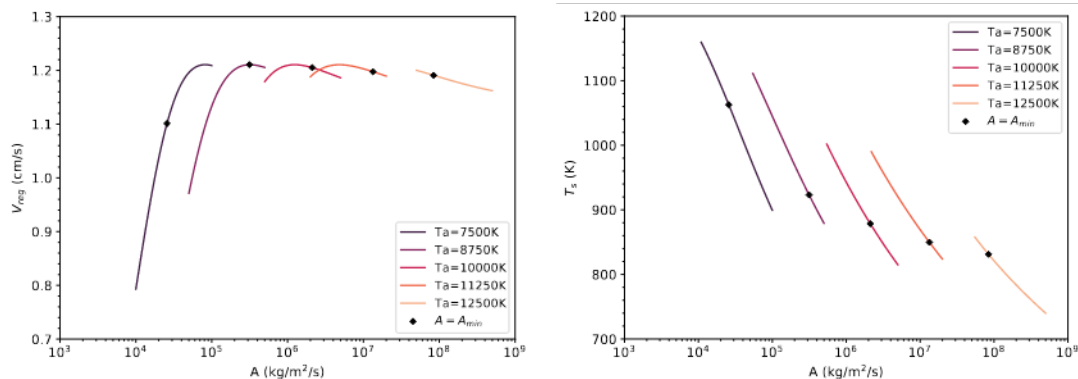


Fig. 16: Calculated regression rate (left) and surface temperature (right) versus pre-exponential factor for different activation temperatures. Ambient pressure 100 atm. Initial condensed-phase temperature 298 K.

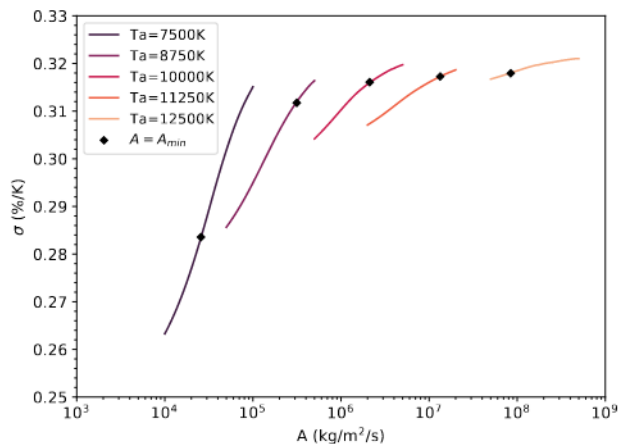


Fig. 17: Calculated sensitivity coefficient versus pre-exponential factor for different activation temperatures. Ambient pressure 100 atm. Initial condensed-phase temperature 298 K.

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  
 363 et al. [5] and Tereshchenko et al. [6]. The species mole fraction profiles, obtained with the present model and  
 364 with the Gross reference model, are compared with the experimental data for the main AP flame products and  
 365 nitrogen-containing species, Figure 18.

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

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

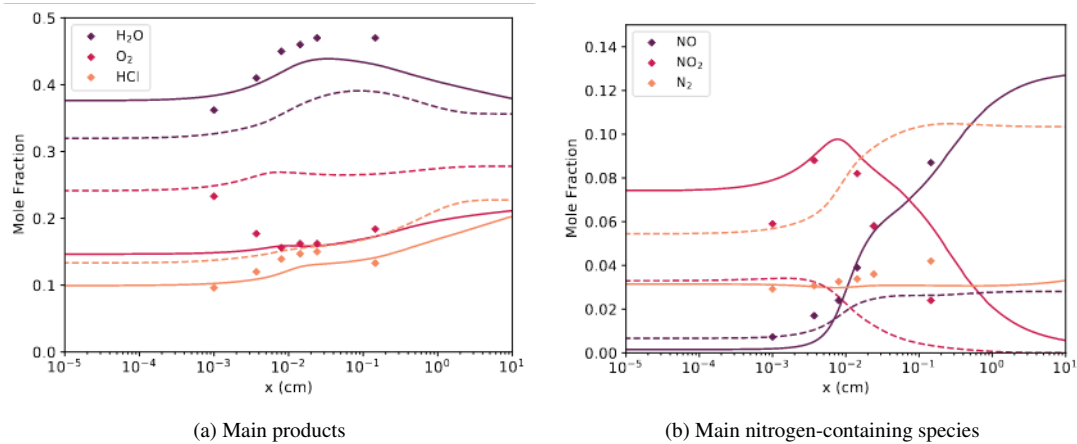


Fig. 18: Species profiles for the AP flame at 0.6 atm and initial temperature 533 K. Symbols: experiment [5]. Solid lines: present model. Dashed lines: Gross model [10].

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

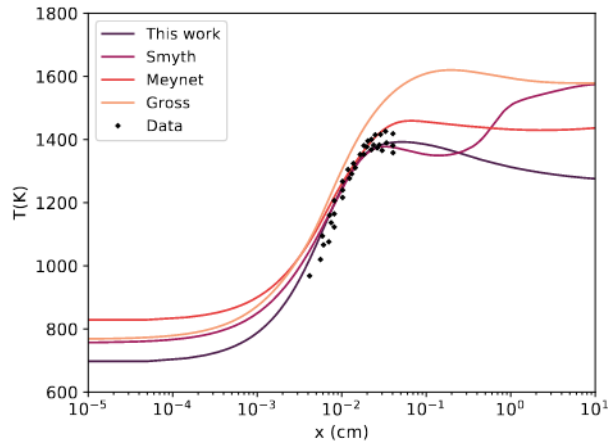


Fig. 19: Temperature profiles in the AP flame at 0.6 atm and initial temperature 533 K. Symbols: experiment [6]. Lines: model prediction.

388 The NO and N<sub>2</sub> profiles predicted with the different models are shown in Figure 20. The observed rapid conversion  
 389 of NO into N<sub>2</sub> 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<sub>x</sub> chemistry. The proposed model, whose NO<sub>x</sub> 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.

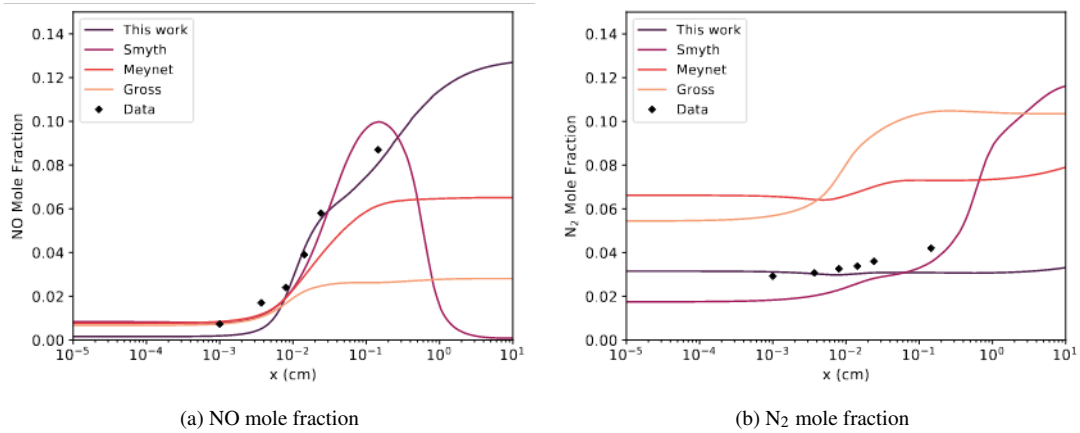


Fig. 20: Profiles of NO and N<sub>2</sub> in the AP flame at 0.6 atm and initial temperature 533 K. Symbols: experiment [5]. Lines: model prediction.

### 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  $\alpha$  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:

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

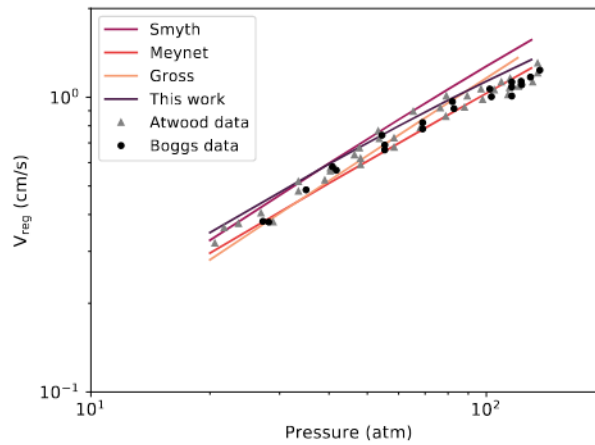


Fig. 21: AP regression rate as a function of pressure. Initial temperature 298 K. Symbols: experiments [1, 38]. Lines: model predictions.

413 Where  $V_{\text{reg}}$  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.

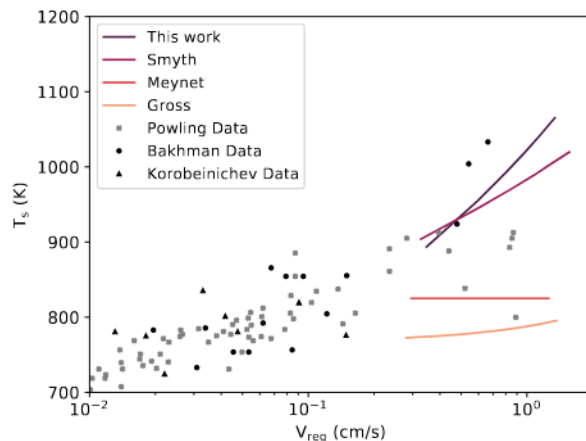


Fig. 22: AP surface temperature as a function of regression rate. Initial temperature 298 K. Symbols: experiments [2–4]. Lines: model prediction.

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 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

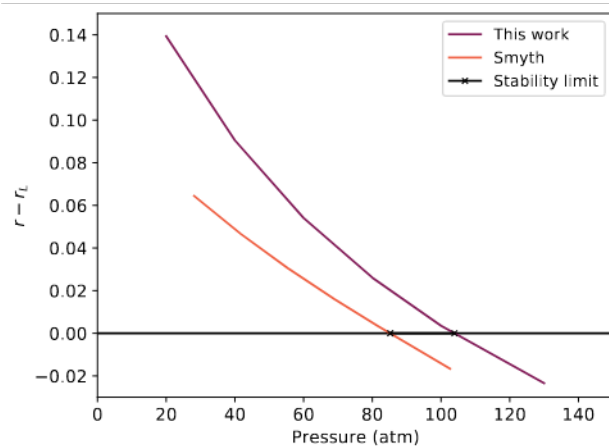


Fig. 23: Stability limit according to the ZN theory for different models.

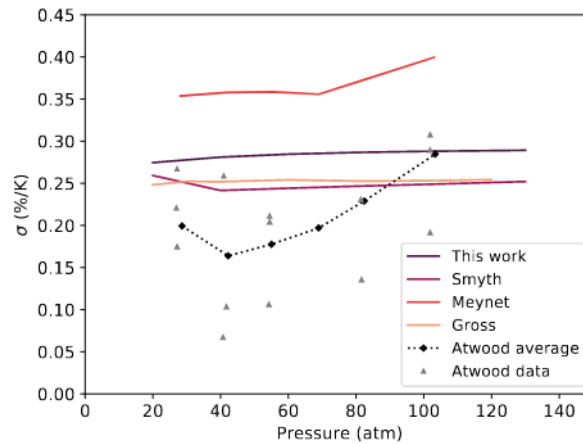


Fig. 24: Temperature sensitivity as a function of pressure. Symbols: experiment [1]. Lines: models [9–11].

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 Cl<sub>2</sub>, *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 H<sub>2</sub>-CH<sub>4</sub>-NH<sub>3</sub>-N<sub>2</sub>O-O<sub>2</sub>-N<sub>2</sub> 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 NO<sub>2</sub> 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 no<sub>2</sub> 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 H<sub>2</sub>+ Cl<sub>2</sub> 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.