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# Gurney and cylinder wall velocities of explosives: analytical estimates and thermochemical simulations†

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Gurney velocity ( $u_G$ ) and cylinder wall velocity ( $v_s$ ) of energetic materials are calculated using the semi-empirical  $C_7$  method, an analytical model previously developed for CHNO high explosives and presently extended to additional elements and to explosives at low loading density. The results are compared to recent procedures based on thermochemical simulations. Regarding  $u_G$ , both approaches perform similarly well for organic high explosives, with an average relative error close to 2.6%. However,  $C_7$  underestimates  $u_G$  for tritonal, an explosive with 20–40 wt% aluminium powder. Regarding  $v_s$ , a newly introduced empirical equation is shown to perform better than the Gurney model, although not as well as a recent correlation involving the detonation energy derived from thermochemical simulations, which are still required to predict cylinder wall velocities with optimal accuracy. With regard to the application of present models to the design of new materials,  $C_7$  is not recommended for metal-containing compounds. However, for the high-throughput design of organic high explosives, it is an invaluable tool allowing fast and reproducible calculations of Gurney energies with state-of-the-art accuracy. A very simple, hackable Python script is provided for this purpose as supplementary information.

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## 1. Introduction

In contrast to thermal stability and sensitivities, the performances of explosives are primarily determined by the difference in properties between their initial unreacted state and the final state of their detonation products.<sup>1,2</sup> As a result, detonation parameters and specific impulses may be accurately estimated from thermochemical simulations.<sup>3–5</sup> However, such performance indicators do not provide any information regarding how fast the material can accelerate the surrounding metal liner. For this purpose, the most used performance indicator is the Gurney velocity  $u_G$ , which is experimentally derived from cylinder wall velocities measured in cylinder expansion tests. This quantity is specially relevant for applications involving the design of shaped charges or other explosive devices that rely on the generation of high-velocity jets or fragments.<sup>6</sup> Prompt values correspond to systems in which confining cases rupture at small expansion, while terminal values correspond to systems in which more ductile case materials

expand further before rupturing.<sup>7</sup> In any case,  $u_G$  critically depends on energy losses, like those occurring as the detonation products fracture the cylinder wall and leak out between the fragments. As a result, it is clear that Gurney velocities cannot be predicted rigorously on the basis of first-principles thermochemical simulations, in sharp contrast to detonation parameters. To get around this difficulty, empirical relationships linking  $u_G$  directly to molecular structure have been reported.<sup>8–10</sup> However, they may exhibit significant errors, as discussed in previous papers.<sup>10–13</sup>

In this context, a more reliable approach was recently put forward by Sućeska and coworkers.<sup>11,12</sup> It relies on the fact that experimental Gurney velocities obtained for a given expansion ratio  $V/V_0$  approximately match  $\sqrt{2E_d}$ , where  $E_d$  is the detonation energy released for a lower value of  $V/V_0$ .<sup>14</sup> This procedure will be hereafter referred to as the EXPLO5 method, since the authors compute  $E_d$  with the help of the eponymous software.<sup>15</sup> In view of its enhanced accuracy compared to empirical methods, it is well suited to case-by-case calculations on a small number of materials. However, as pointed out by Jeremić and Bogdanov,<sup>16</sup> it also has a number of drawbacks. First, the output of thermochemical codes depends on many parameters describing the properties and equation of state of the detonation products, which hampers cross-comparisons between simulations made with different codes, or even with different versions of the same code. Secondly, as a proprietary software, the EXPLO5 code is only available to engineers who have a

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† Electronic supplementary information (ESI) available: PDF file with discussion of dubious experimental data and in-depth validation of the  $C_7$  model, including Tables S1–S3; Excel file compiling Gurney energies (Table S4), relevant material properties (Table S5) and cylinder wall velocities (Table S6); Python script for quick and easy application of the  $C_7$  model. This supporting information may be found in the online version of the article at the publisher's website. See DOI: <https://doi.org/10.1039/d5cp00761e>



sufficiently recurring need for it to justify its purchase. More generally, current thermochemical software is limited in availability for reasons of cost and/or confidentiality. Finally, such codes typically describe the gaseous detonation products using the Becker–Kistiakowsky–Wilson (BKW) equation of state (EoS), whose mathematical formulation is computationally expensive and requires the gas composition to be iteratively determined *via* an appropriate chemical equilibrium solver.<sup>17</sup> While this is no significant issue for a chemist in need of performance data for a few molecules he has in mind, this becomes more of a problem in the context of modern approaches to the design of energetic materials based on large scale screening of the chemical space.<sup>18</sup> Indeed, with the availability of extremely efficient models to estimate crystal density,<sup>19,20</sup> heat of formation,<sup>21,22</sup> and to a lesser extent sensitivity<sup>23,24</sup> and thermal stability,<sup>25,26</sup> the search for the equilibrium composition and properties of the detonation products stands out as a major bottleneck in the high-throughput assessment of explosives.

Fortunately, this costly step can be avoided using simple rules of thumb regarding the composition of the detonation products.<sup>16,27</sup> For instance, it was recently shown<sup>28</sup> that detonation parameters can be predicted with very good reliability and for a wide range of explosive compositions using the H<sub>2</sub>O–CO<sub>2</sub> arbitrary introduced by Kamlet and Jacobs, *i.e.* the following hierarchy in product formation: H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, C and H<sub>2</sub>. Regarding prediction of Gurney velocities, the same rule is used by an earlier analytical model referred to as C<sub>γ</sub>,<sup>13</sup> where the name refers to the fact that this model starts from an equation obtained assuming a polytropic expansion of the detonation products in the case where the polytropic index  $\gamma$  is constant. As detailed in ref. 13, C<sub>γ</sub> predicts Gurney velocities with much better reliability than earlier empirical methods, with a reduction in the average error by a factor of between 2 and 3, depending on the expansion rate considered. Therefore, it would be interesting to compare the EXPLO5 procedure to C<sub>γ</sub>, as the former has previously been compared solely to crude empirical methods, whereas the latter is more convenient for engineering applications and more widely available as it requires only paper and pencil. This comparison is the goal of the present paper.

## 2. Detailed procedures

Full details of the EXPLO5 and C<sub>γ</sub> procedures compared in this work may be found respectively in ref. 12 and 13. For completeness, a brief outline is provided below.

### 2.1. EXPLO5 procedure

The EXPLO5 procedure described in ref. 11 and 12 is based on the empirical observation that the detonation energies calculated at about threefold expansion of the products matches very well with experimental Gurney energies. More specifically,  $E_G$  is assumed to be proportional to the detonation energy calculated for an expansion ratio  $V/V_0 = 3$ :

$$E_G \propto E_d(V/V_0 = 3) \quad (1)$$

In principle, the proportionality coefficient depends on the expansion ratio considered. It proves very close to unity for small expansion ratios, for which the approach proves especially successful, with a determination coefficient  $R^2$  as large as 0.95 between estimated and observed  $u_G$  values.<sup>12</sup>

### 2.2. C<sub>γ</sub> model

In contrast to most empirical methods,<sup>8–10</sup> the C<sub>γ</sub> model derives  $u_G$  from the Gurney energy  $E_G = u_G^2/2$ , defined as follows:

$$E_G = E_0 - E_s(V/V_0) \quad (2)$$

where  $E_0$  is the value of the detonation energy  $E_d$  at infinite volume, and  $E_s$  is the part of this chemical energy that does not contribute to accelerate the driven metal, *i.e.* the internal energy remaining in the detonation products as their expansion ratio equals  $V/V_0$ .

The C<sub>γ</sub> model was initially introduced in ref. 13 on the basis of an isentropic expansion of the decomposition products involving a polytropic exponent  $\gamma$ . As its name implies, this model starts with the assumption of a constant  $\gamma$ . This leads to the following equation for the Gurney energy:<sup>13</sup>

$$E_G = E_0 \left[ 1 - 2 \left( \frac{V_0}{V} \right)^{\gamma-1} \left( \frac{\gamma}{\gamma+1} \right)^\gamma \right] \quad (3)$$

The dependence of  $\gamma$  on the expansion ratio is re-introduced in a second step, by using distinct values of  $\gamma$  for data sets corresponding to different  $V/V_0$  values. The effective value to be used in eqn (3) is estimated on the basis of the loading density  $\rho_0$  and number of moles  $N$  of gaseous species produced per gram of explosive:

$$V/V_0 = \nu \times \rho_0 N \quad (4)$$

where the proportionality constant  $\nu$  is homogeneous to a volume. Any potential dependence of  $\gamma$  and  $\nu$  on the nature of the expanding gases and solid particles is neglected. This allows these two quantities to be fitted against experimental  $u_G$  data for any value of the observed expansion ratio. They can then be used to predict Gurney velocities for new materials.

This simple procedure may be alternatively obtained without reference to a polytropic expansion, simply assuming that the energy that does not contribute to the metal acceleration is a fraction of  $E_0$  that depends on the expansion ratio as  $(V_0/V)^\eta$  with an adjustable proportionality constant and an empirical exponent  $\eta$  that do not depend on the chemical composition of the explosive.

In principle, having estimated the Gurney velocity  $u_G$  using the method described above, the cylinder wall velocity  $v_s$  to be expected from cylinder test experiments can be calculated using the Gurney model in reverse. This is especially straightforward in the configuration of such experiments, due to the simple cylindrical geometry involved:

$$v_s = \sqrt{2E_G} \left( \frac{1}{2} + \frac{M_C}{M_E} \right)^{-1/2} \quad (5)$$

where  $M_C/M_E$ , which stands for the ratio of the weight of the copper cylinder to the weight of the explosive sample, is obtained as  $(4.033 \text{ g cm}^{-3})/\rho_0$ , as detailed in ref. 12.



In the present work, unless mentioned otherwise, we use previously introduced parameters  $\gamma = 2.3$  and  $\nu = 37 \text{ cc mol}^{-1}$  that proved suitable to estimate terminal Gurney velocities,<sup>13</sup> which are more important in practice than prompt values.<sup>10</sup> On the other hand, to make the model applicable to additional elements beyond CHNO, an extended hierarchy is used regarding product formation. Namely,  $\text{Al}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{NaCl}$ ,  $\text{HF}$ ,  $\text{CF}_4$ ,  $\text{HCl}$ ,  $\text{CCl}_4$  are assumed to be produced before the  $\text{H}_2\text{O}-\text{CO}_2$  arbitrary is applied. The formation enthalpies required as input to the calculations were preferably taken from the original ref. 4, 10 and 29–33 otherwise from the Dobratz explosive handbook.<sup>7</sup>

### 2.3. $C_\gamma$ versus EXPLO5 comparison

This work compares the outcome of  $C_\gamma$  and EXPLO5 regarding Gurney velocities at terminal expansion compiled by EXPLO5 developers.<sup>11,12</sup> The predictive value of both methods is primarily assessed on the basis of root mean square error (RMSE) data in  $\text{km s}^{-1}$ , and corresponding value  $\delta$  in percent, following ref. 13.

Previously introduced data sets are used, namely the Stimac *et al.* data set from ref. 11 and the Sućeska *et al.* data set from ref. 12. The names and corresponding structures of the explosives presently considered may be found in these two papers. For completeness, they are also reported in ESI,<sup>†</sup> along with presently used values of the formation enthalpies. It should be noted that since the latter were obtained from third-party literature, they could possibly differ from the values assumed in the reference EXPLO5 calculations.<sup>11,12</sup> We focus on organic explosives for two reasons.

First, in view of its reliance on the  $\text{H}_2\text{O}-\text{CO}_2$  arbitrary, the current  $C_\gamma$  model is in principle specially well-suited to CHNO compounds. In contrast, its application to aluminium-containing explosives is more questionable as we systematically assume Al to be completely converted in  $\text{Al}_2\text{O}_3$ . Similar ambiguities arise for any metal-containing explosive.

Secondly, the data reported in ref. 12 does not make it possible to account for the wide variability of ANFO data, that might arise as a result of experimental uncertainties and possible differences in the precise composition of the materials. Indeed, several inconsistencies may be noted regarding this data. For instance, regarding Gurney velocities of ANFO, ref. 12 reports a value of  $2.14 \text{ km s}^{-1}$  at  $0.82 \text{ g cc}^{-1}$  taken from Fedoroff<sup>29</sup> and a much lower value of  $1.63 \text{ km s}^{-1}$  at  $0.83 \text{ g cc}^{-1}$  that could not be found in the reference cited.<sup>34</sup> As a result, it is not possible for us to draw any reliable conclusion from the data reported for ammonium nitrate (AN) based explosives.

## 3. Results

### 3.1. Validation of the $C_\gamma$ equation

Keeping in mind the fact that  $\nu$  and  $\gamma$  are fitted against experiment, the  $C_\gamma$  equations may be alternatively derived without reference to the polytropic exponent  $\gamma$ , simply assuming that the internal energy  $E_s = E_0 - E_G$  of the detonation products decreases with the molar density  $\rho_0 N$  according to a power law with exponent  $\eta$ , in other words:

$$E_s/E_0 = k/(\rho_0 N)^\eta \quad (6)$$

where the two parameters  $\eta$  and  $k$  may be fitted against experiment, or equivalently obtained from previously fitted values of  $\nu$  and  $\gamma$  as  $\eta = \gamma - 1$  and:

$$k = 2\left(\frac{1}{\nu}\right)^{\gamma-1} \left(\frac{\gamma}{\gamma+1}\right)^\gamma \quad (7)$$

Therefore, the above mentioned  $C_\gamma$  assumption (eqn (6)) is equivalent to assuming a linear decrease of  $\log[1 - E_G/E_D(\infty)]$  with  $\log(\rho_0 N)$ . The validity of this assumption is checked in Fig. 1 using all data reported by Stimac *et al.*<sup>11</sup> for a set of 39 measurements carried out for various organic explosives and loading densities.  $C_\gamma$  may be readily applied to this data set as most compounds included in it contain only CHNO elements, except for three formulations (LX-04, LX-09 and LX-10) with negligible amounts of fluorine in the binder.

Even in the case of such organic high explosives for which an ideal detonation behavior is expected, it is clear that experimental data found in this compilation exhibit significant uncertainties, especially when considering values taken from different sources. For instance, three experimental values are reported for the Gurney velocity of Comp B at a density  $\rho_0 = 1.72 \text{ g cc}^{-1}$ , namely values  $u_G = 2.71 \text{ km s}^{-1}$  and  $u_G = 2.79 \text{ km s}^{-1}$  taken from Locking<sup>10</sup> and a value  $u_G = 2.80 \text{ km s}^{-1}$  taken from Fedoroff.<sup>29</sup> The deviation of about 3.6% between extremal values is larger than the root mean square deviation of 3.28% reported between measured and estimated values,<sup>11</sup> which clearly shows that experimental uncertainties may significantly contribute to such statistical indicators. Similarly, considering the value  $u_G = 2.79 \text{ km s}^{-1}$  taken from Locking for cyclotol 77/23, a slightly lower value might be expected for cyclotol 75/25 in view of its slightly reduced fraction of RDX. For the latter material, a larger value  $u_G = 2.86 \text{ km s}^{-1}$  is actually found

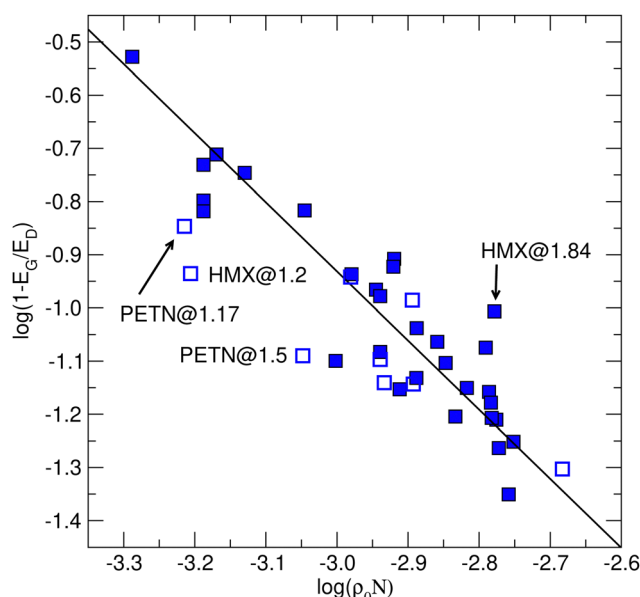


Fig. 1 Values of  $\ln[1 - E_G/E_D(\infty)]$  plotted as a function of  $\ln(\rho_0 N)$  for the 39 entries considered in ref. 11, including Locking (full symbols) as well as Fedoroff (empty symbols) data. Labels indicate the name of the explosive along with the corresponding density ( $\text{g cc}^{-1}$ ).



in Fedoroff encyclopedia.<sup>29</sup> Therefore, we presently consider Locking and Fedoroff entries separately, keeping in mind that experimental uncertainties of about  $0.1 \text{ km s}^{-1}$  are to be expected. A distinctive feature of the Fedoroff subset is that it includes data measured for very low loading densities, namely for HMX at a density of  $1.2 \text{ g cc}^{-1}$  and for PETN at densities of  $1.27$  and  $1.5 \text{ g cc}^{-1}$ .

Despite uncertainties inherent to present data, Fig. 1 does confirm the validity of the correlation at the basis of  $C_\gamma$ . However, Fedoroff entries corresponding to high explosives at reduced loading densities tend to fall away from the main trend. For such samples, the low density stems from the occurrences of voids in the sample. Since these voids get closed as a shock is applied to the system, the significance of the initial loading density when it comes to describing the detonation products is questionable.

### 3.2. Generalizing $C_\gamma$ to reduced loading densities

Fig. 2 shows the drop in  $u_G$  on going from a loading density close to the theoretical maximal density (TMD) of the crystal to reduced loading densities. In contrast to both  $C_\gamma$  and EXPLO5 procedures that predict an approximately linear decrease of  $u_G$  on going to smaller  $\rho_0$  values, experiments suggest a qualitative change from a convex to a concave dependence on going from HMX to PETN, possibly due to the uncertainties inherent to such measurements. In any case, Fig. 2 strongly suggests that the drop in  $u_G$  on going to much reduced loading densities is overestimated by both models. We might attribute this to the neglect of the collapse of the porosity as the sample is primed.

For the 30 entries taken from Locking, this systematic error does not show up as this data set does not include any experiment at low explosive density. Therefore, EXPLO5 is about as good as  $C_\gamma$  on average, as reflected by  $\delta$ -values of

respectively 2.9% and 2.5%. Gurney velocities fall systematically within 6% from experiment using both models, except for TACOT for which  $u_G$  is overestimated by almost 8% using  $C_\gamma$  and over 10% using EXPLO5, as already noted by Stimac *et al.*<sup>11</sup> As pointed out by a reviewer and detailed in ESI,<sup>†</sup> the experimental value of  $2.12 \text{ km s}^{-1}$  reported for TACOT appears to be the prompt instead of terminal value, which should be in the range  $2.30$ – $2.40 \text{ km s}^{-1}$  according to careful estimates, in fair agreement with the values of  $2.28$  and  $2.34 \text{ km s}^{-1}$  calculated using  $C_\gamma$  and EXPLO5, respectively.

In contrast, Fedoroff data includes measurements carried out for reduced loading densities, as mentioned above, and for which  $u_G$  is severely underestimated. For instance, both models predict a velocity of  $2.71 \text{ km s}^{-1}$  for PETN at  $1.5 \text{ g cc}^{-1}$ , much lower than the measured value of  $2.9 \text{ km s}^{-1}$ . This flaw is especially serious for  $C_\gamma$ , leading to even more serious errors for extremely low densities:  $-10.6\%$  for HMX at  $1.2 \text{ g cc}^{-1}$  and  $-8.4\%$  for PETN at  $1.27 \text{ g cc}^{-1}$ . The much too small velocities predicted in such cases is reflected by  $\delta$  values as large as  $4.4\%$  for EXPLO5 and  $5.3\%$  for  $C_\gamma$ . Considering the whole Stimac data set including Locking as well as Fedoroff entries, both  $C_\gamma$  and EXPLO5 yield similar performance with  $\delta = 3.3\%$ , proving satisfactory on average except for reduced loading densities.

Using the  $C_\gamma$  model, a simple empirical way to mitigate the too fast decrease in  $u_G$  on considering reduced loading density is to replace  $\rho_0$  by the geometric mean  $\sqrt{\rho_0 \rho_{\text{max}}}$  in the equations, where  $\rho_{\text{max}}$  is the TMD, when available, otherwise the largest density obtained in cylinder wall experiments for the material considered. In so doing,  $\delta$  increases from  $2.5\%$  to  $2.9\%$  for the Locking subset which does not contain any measurement at very low density. However, for the nine Fedoroff measurements,  $\delta$  drops from  $5.3\%$  down to  $1.9\%$ .

### 3.3. Further assessment of Gurney velocities

After it was originally introduced by Stimac *et al.*<sup>11</sup> the EXPLO5 approach was subsequently compared to additional data sets from the same group of Sucasca *et al.*<sup>12</sup> These data sets, compiled in Table 1 of ref. 12, include high explosives, ammonium nitrate-based non-ideal explosives, and aluminized explosives.

In this section,  $C_\gamma$  is assessed against this comprehensive data set. The TMD scaling described in Section 3.2 is systematically applied to experiments made at reduced loading densities. All results are compiled in Table S4 (ESI<sup>†</sup>), using data from Table S5 (ESI<sup>†</sup>), and summarized in Fig. 3. Although the model was originally designed for ideal high explosives, a good agreement with experiment is obtained for all data taken from

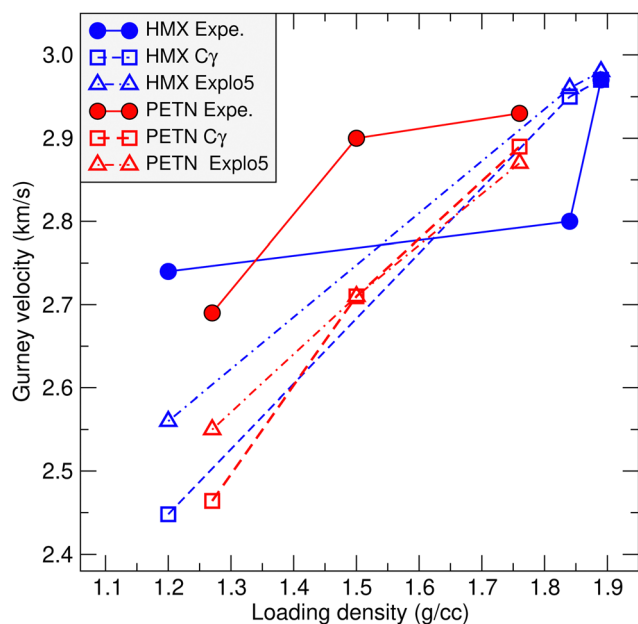


Fig. 2 Drop in Gurney velocity  $u_G$  on going to reduced loading densities.

**Table 1** Parameters used to derive cylinder wall velocities as a function of the  $V/V_0$  ratio, including  $\gamma$  (dimensionless) and  $\nu$  ( $\text{cm}^3 \text{ mol}^{-1}$ ) values required to apply the Gurney model, as well as  $\rho_c$  ( $\text{g cm}^{-3}$ ) and  $u_c$  ( $\text{km s}^{-1}$ ) parameters involved in eqn (8)

$V/V_0$	$\gamma$	$\nu$	$\rho_c$	$u_c$
2.2	$1.73 \pm 0.07$	$43.4 \pm 3.1$	$4.496 \pm 0.032$	$0.40 \pm 0.03$
3.9	$1.99 \pm 0.09$	$43.7 \pm 3.0$	$4.305 \pm 0.041$	$0.49 \pm 0.04$
6.2	$2.14 \pm 0.10$	$43.9 \pm 2.8$	$4.202 \pm 0.044$	$0.53 \pm 0.04$





the Fedoroff compilation, including materials made of ammonium nitrate mixed with RDX or TNT and two ANFO slurries. Larger deviations may be observed for data taken from alternative sources, which comes as no surprise due to a lack in information regarding the details of the compositions studied and the apparent inconsistencies in the experimental data, as discussed above in Section 2.3 for ammonium-based explosives (ANFO) and in Section 3.1 for high explosives.

In view of applying  $C_\gamma$  to the nine Al-containing explosives introduced in ref. 12, Al is assumed to be fully converted to  $\text{Al}_2\text{O}_3$ . This yields good predictions, except for tritonal, a mixture of 80% TNT and 20% Al for which  $u_G$  is dramatically underestimated, as shown in Fig. 3. Upon closer examination, it may be noted that the specially low Gurney velocity predicted for this material arises because the present  $\text{Al}_2\text{O}_3\text{-H}_2\text{O-CO}_2$  arbitrary yields a specially small amount of gases evolved from combustion, namely  $0.025 \text{ cc g}^{-1}$ , versus over  $0.3 \text{ cc g}^{-1}$  for HTA-3 and HBX-3, two materials with an even larger Al weight fraction. Consequently,  $E_G$  represents only about 7% of the total detonation energy for tritonal, versus about 30% for HTA-3 and HBX-3. Given the complexities induced by Al particles in non-ideal explosives,<sup>35</sup> there is presently no simple and reliable model to predict the performances of such materials without resorting to numerical simulations.

The remaining 43 high explosives represent in principle a more challenging data test set for  $C_\gamma$  compared to the Stimac *et al.* data set considered above. This is due to the occurrence of fluorine compounds, as well as explosives with Al/Ba in significant amounts. In order to handle those elements with  $C_\gamma$ , all fluorine and aluminium atoms are assumed to be converted

to HF and  $\text{Al}_2\text{O}_3$ , respectively. For these compounds, both  $C_\gamma$  and EXPLO5 performs about equally well on average. The small increase in  $\delta$  observed by comparison with the Stimac *et al.* data set (from 3.3% to 3.6%) stems from the addition of more challenging data, namely baratol, an explosive including barium nitrate, for which  $u_G$  is predicted too small by about 8%, and measurements at reduced loading densities of about  $1.5 \text{ g cc}^{-1}$  (EDD, HNS) for which  $u_G$  is predicted too low, especially for HNS, an explosive with a very negative oxygen balance (−68%) and for which the loading densities of 1.2 and  $1.6 \text{ g cc}^{-1}$  are much lower than the theoretical maximal density (TMD) of  $1.75 \text{ g cc}^{-1}$ .<sup>36</sup>

The experimental velocity for baratol should be considered with caution as it was derived using a 1D (flyer plate) configuration, in contrast to all other data which were obtained using a 2D (cylinder) configuration.<sup>37</sup> Anyway, the measured value of  $1.62 \text{ km s}^{-1}$  being specially small, the relative deviation of 8% corresponds in fact to a difference of only  $0.12 \text{ km s}^{-1}$  between measured and calculated velocities.

Finally, Gurney velocities were calculated using  $C_\gamma$  for a set of nine additional explosives for which experimental  $u_G$  data were reported in miscellaneous sources brought to our attention by a reviewer.<sup>38–44</sup> In some cases, a number of distinct plausible values could be found for their formation enthalpies and were used in the calculations. See ESI† for further details and references.† The overall results are summarized in Fig. 4.

In this Figure, the vertical lines link symbols corresponding to distinct calculations for the same material, differing only in the input value assumed for the formation enthalpy. This demonstrates the relatively moderate role of the uncertainties on formation enthalpies.

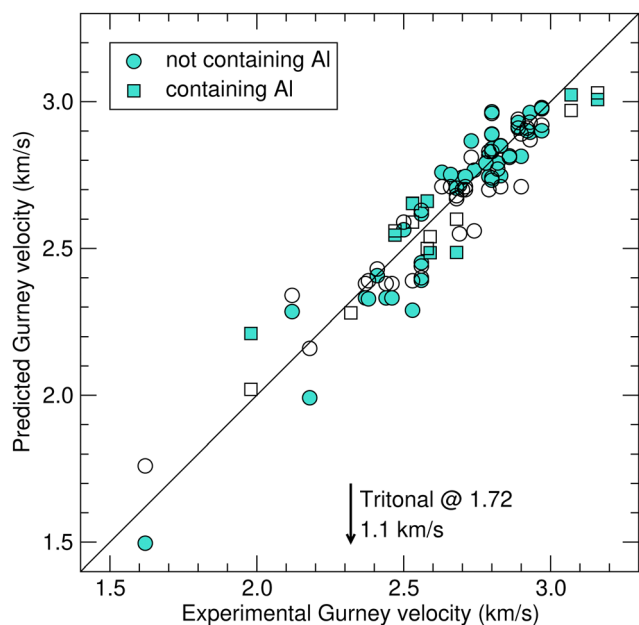


Fig. 3 Comparison of predicted versus measured Gurney velocities for explosives without (circles) and with (squares) Al. Calculations are made using  $C_\gamma$  (turquoise symbols) and EXPLO5 (empty symbols).  $C_\gamma$  predicts a value  $u_G = 1.1 \text{ km s}^{-1}$  for Tritonal (not shown) much smaller than the experimental value of  $2.32 \text{ km s}^{-1}$ .

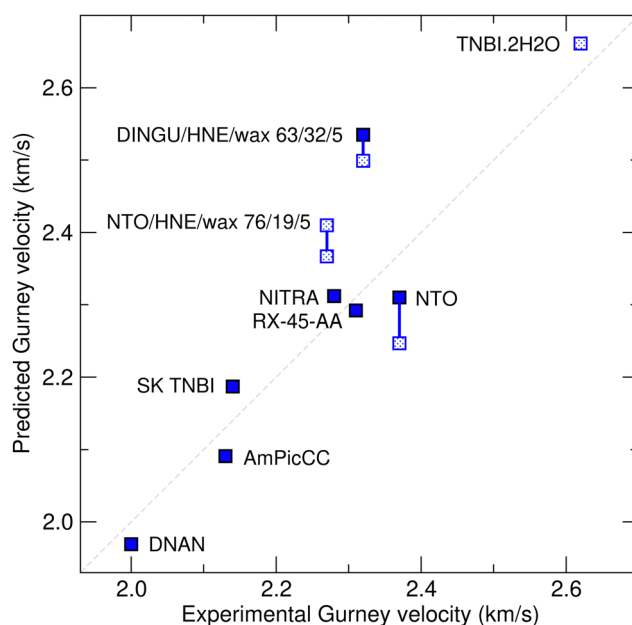


Fig. 4 Comparison of predicted versus measured  $u_G$  data reported in earlier studies.<sup>38–44</sup> Calculations are made using formation enthalpies either suggested by the reviewer (close symbols) or presently retrieved from standard compilations<sup>45,46</sup> (open symbols) as detailed in ESI.†



Considering only the seven explosives with formation enthalpies suggested by the reviewer (close symbols), an average relative error of 2.8% is obtained. As clear from Fig. 4, the most significant deviation is observed for DINGU/HNE/wax, a formulation based on dinitroglycoluril (DINGU) and hexanitroethane (HNE) with wax as binder. Hypothesizing that the value of  $-47 \text{ kJ mol}^{-1}$  used for this formulation was overestimated, we calculated an alternative value from the enthalpies of its individuals constituting species (see ESI†). However, no significant reduction of the discrepancy between calculation and experiment could be obtained for this formulation.

This prompted us to estimate  $u_G$  for a somewhat similar formulation reported by the same author,<sup>44</sup> namely NTO/HNE/wax. Two values were obtained, corresponding to the two experimental formation enthalpies of  $-101$  and  $-129.4 \text{ kJ mol}^{-1}$  reported for NTO,<sup>45</sup> leading to an overestimated  $u_G$  in both cases. Interestingly,  $u_G$  is specially overestimated for the two HNE-containing formulations, with an apparent correlation between deviation from experiment and weight fraction of HNE, suggesting issues associated with the latter compound, whose structure  $(\text{NO}_2)_3\text{C}-\text{C}(\text{NO}_2)_3$  is unique.

### 3.4. Cylinder wall velocities

The ability of  $C_\gamma$  to predict Gurney velocities with an accuracy comparable to that of numerical simulations warrants its application, along with the Gurney model (eqn (5)), to the problem of calculating cylinder wall velocities  $v_s$ . This involves an adjustment of the model parameters  $\gamma$  and  $\nu$  so as to reflect the  $V/V_0$  values of 2.2, 3.9 and 6.2 considered in this study. The newly optimized parameters are compiled in Table 1. The corresponding results thus obtained are compiled in Table S6 (ESI†) and shown in Fig. 5a.

As clear from this figure, two liquids stand out as outliers, namely 1,2-bis(difluoroamino)propane or 1,2-DP (blue symbols) and tetranitromethane or TNM (red symbols). The large deviations from experiment observed for these compounds are all the more puzzling as  $v_s$  is reasonably well predicted for the two other liquid compounds in the database, namely nitromethane and FEFO. In fact, notwithstanding 1,2-DP and TNM, cylinder wall velocities are reasonably well described overall, with an average relative error of about 2%. Nevertheless, a deviation from experiment close to 10% is observed for PETN.

Therefore, following ref. 12, we consider empirical alternatives to the Gurney model (eqn (5)) to estimate cylinder wall velocities. However, present analytic estimates of  $E_d$  do not allow us to reproduce the striking correlation between  $v_s$  and  $\sqrt{\rho_0 E_d}$  reported by these authors using simulated  $E_d$  data. In contrast, our best model for  $v_s(V/V_0)$  consists in a linear relationship with  $\rho_0 u_G$ , namely:

$$v_s(V/V_0) = (\rho_0/\rho_c)u_G + u_c \quad (8)$$

where the characteristic density  $\rho_c$  and velocity  $u_c$  are model parameters that depend on the expansion ratio  $V/V_0$  under consideration. Their values are reported in Table 1.

The  $v_s$  estimates thus obtained are compiled in Table S6 (ESI†) and plotted against experimental values in Fig. 5b.

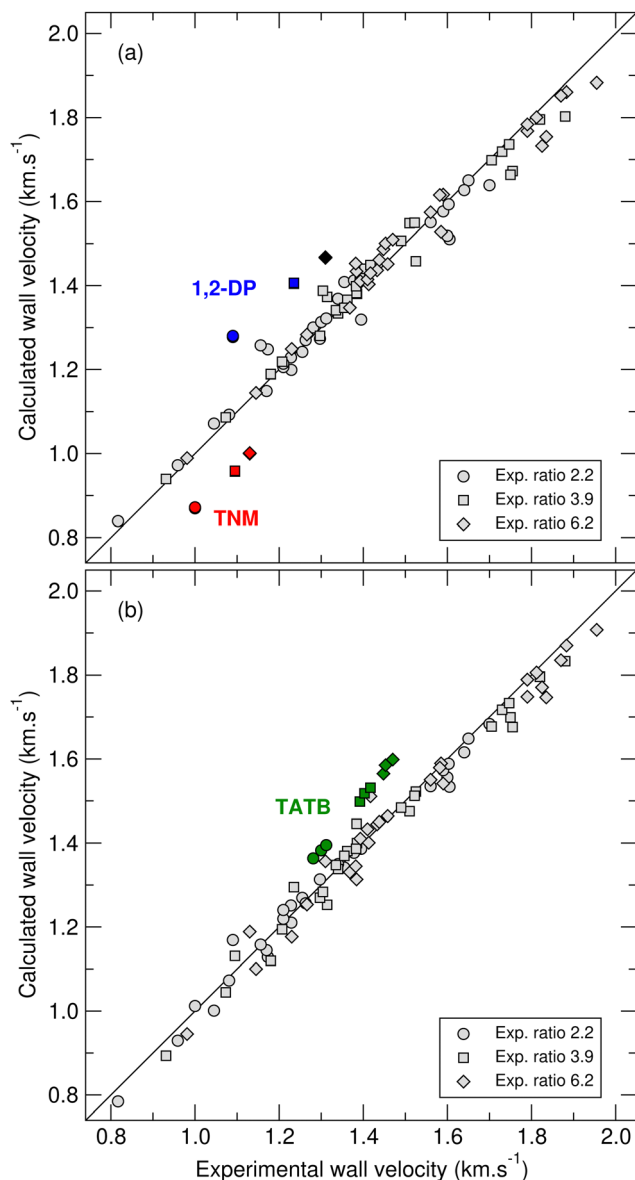


Fig. 5 Estimated cylinder wall velocities plotted against experimental values. Circles, squares and diamonds represent data for  $V/V_0$  values of respectively 2.2, 3.9 and 6.2. Estimated values obtained: (a) using the Gurney and  $C_\gamma$  models; (b) using the correlation involving density and Gurney velocity (eqn (8)). Table 1 compiles all parameters involved. See text for further details.

Interestingly, the measured data for 1,2-DP and TNM are satisfactorily predicted by eqn (8). The only significant outlier observed using this equation is triaminotrinitrobenzene (TATB) for which  $v_s$  is consistently overestimated (green symbols in Fig. 5b). Just like 1,2-DP, trinitrotoluene (TNT) and hexanitrostilbene (HNS), this compound is largely sub-oxygenated, with an oxygen balance (OB) below  $-50\%$ . Accurately assessing the performance of such compounds has always been a challenge because they often deviate from the ideal behavior upon which the classical Chapman–Jouguet (CJ) detonation theory and most current thermochemical codes for explosive performances are based. Furthermore, TATB exhibits higher nitrogen content

compared to most explosives with  $OB < -50\%$ , including those in the present data set. In fact, it was recently reported that TATB soot substantially differs from other high explosives.<sup>47</sup> More specifically, the authors showed that recovered soot of a polymer-bonded TATB sample exhibits a nitrogen-carbon molar ratio N/C as high as 0.25, compared to 0.03 for other explosives of practical interest. They showed evidence that N-trapping in TATB soot is likely to be responsible for detonation parameters to be lower than predicted from thermochemical simulations.

In view of these complications, and given that TATB also stands out among well-studied explosives for its large porosity,<sup>48</sup> the fact that the EXPLO5 correlation predicts the corresponding cylinder wall velocity with good precision is quite remarkable.

## 4. Conclusions

Two approaches to the evaluation of explosive performances were compared regarding their abilities to predict Gurney velocity ( $u_G = \sqrt{2E_G}$ ) and cylinder wall velocity ( $v_s$ ) using stoichiometry, formation enthalpy and loading density as only inputs.

The first one, called EXPLO5 in this article, is based on numerical simulations of cylinder test experiments performed using the eponymous thermochemical code. The latter provides an accurate description of the expanding products and the corresponding values of the detonation energy  $E_d$  as a function of the expansion ratio  $V/V_0$ . The Gurney and cylinder wall velocities are then obtained from linear correlations with computed values of  $E_d(V/V_0 = 3)$  and  $\sqrt{\rho_0 E_d(V/V_0)}$ , respectively.

The second one, named  $C_\gamma$ , relies on the detonation products as obtained on the basis of the  $H_2O-CO_2$  arbitrary. Therefore, in contrast to EXPLO5, it cannot describe the detonation products as they expand. The prompt and terminal Gurney energies are instead calculated using simple analytic expressions derived from the assumption of a polytropic expansion of the detonation products and fitted against experiment.

Regarding the comparison of the two methods, inconsistencies in experimental data at hand do not allow us to draw definite conclusions for ammonium nitrate-based explosives. However, for metal-rich explosives, the current  $C_\gamma$  parameterization is clearly inappropriate and should not be used, as demonstrated by the dramatic error observed for tritonal.

This analytic model is actually focused on CHNO high explosives. However, due to the use of the  $H_2O-CO_2$  arbitrary instead of rigorous thermochemical simulations, it can only estimate the final equilibrium composition of the products and the corresponding enthalpy, in contrast to EXPLO5 that provides such data as a function of  $V/V_0$ . This prevents the accurate determination of cylinder wall velocities through the  $\sqrt{\rho_0 E_d(V/V_0)}$  correlation. In fact, an alternative linear correlation with  $\rho_0 u_G$  as descriptor proves more successful when using  $C_\gamma$  data as input. In any case, both correlations prove more successful than application of the Gurney model (eqn (5)).

Finally, the detonation parameters calculated by thermochemical codes as a function of the expansion ratio of the products

prove invaluable inputs in view of predicting Gurney and cylinder wall velocities with optimal accuracy. However, despite a more restricted scope, the  $C_\gamma$  model provides an equally accurate and more efficient alternative. An interactive Python script is provided as ESI† for easy application of the model. Using a similar script, Gurney velocities can be estimated at a rate of about 50 k materials per second, which is of major interest in the context of high throughput virtual screening of organic high explosives. However, the main bottleneck in the accurate prediction of detonation performances lie in the efficient evaluation of gas-phase formation enthalpies for the molecules. Indeed, although fast methods are available for this purpose, based either on additivity considerations<sup>49</sup> or machine learning,<sup>50</sup> they are still lacking in accuracy compared to high level *ab initio* methods for some families of compounds.<sup>51,52</sup>

Nevertheless, even when more costly quantum chemical calculations are used to obtain the enthalpy of formation with optimum accuracy, cancelling out the  $C_\gamma$  advantage in terms of efficiency, there are a number of reasons why this model may be preferred over EXPLO5. First, in contrast to the many parameters required to describe the expanding products in thermochemical codes,  $C_\gamma$  requires just two empirical parameters to predict terminal Gurney velocity, thus avoids annoying variations in results due to different parameterizations. Secondly, being trivial to implement,  $C_\gamma$  may be straightforwardly integrated into any existing workflow, for instance downstream of molecule generation algorithms in the context of high-throughput virtual screening of the chemical space.

## Data availability

The data supporting this article have been included as part of the ESI,† including all input data and results of present calculations and a Python script for easy application of the  $C_\gamma$  model to Gurney velocity prediction.

## Conflicts of interest

The authors declare no potential conflict of interests.

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