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Predictive model of explosive detonation parameters from an equation of state based on detonation velocity[†]

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This article describes a predictive model of explosive detonation velocity and pressure based on first-order approximation of the detonation velocity equation. Detonation pressure was calculated from equations derived from the ideal detonation theory since that pressure is functionally related to detonation velocity. In the model calibration process, several product formation hierarchies were explored, with the best results yielded by the Kamlet and Jacobs (KJ) hierarchy. The predictive capacity of our model (labelled DEoS) was tested using different experimental databases, and was compared with predictions by thermochemical models (BKW-RR, JCZ3-J and JCZS) and by the empirical KJ method. The prediction values obtained using an experimental database of 238 explosive substances (75 singles and 163 composites), for a range of densities (1 g/cc to 2 g/cc), were excellent in terms of both velocity and pressure, with root mean square error values of 1.7% (519 data items) and 6.0% (263 data items), respectively. We analysed results, broken down by explosive type, in detail, finding that the model residuals did not correlate with the predictor variables and also that the model predicts reasonable values for other parameters in the detonation state, such as density, the Jones parameter, and the Grüneisen parameter.

1 Introduction

The search for new substances and compositions for high-performance explosives has motivated the development of several models to predict the velocity (D) and pressure (P) of explosive detonations^{1–17}.

Some models use equations derived from the ideal detonation theory (IDT) to formulate thermochemical equations of state (EoS) that determine the composition and thermodynamics of detonation products, e.g., the Becker-Kistiakowsky-Wilson (BKW)² and the Jacobs-Cowperthwaite-Zwisler-3 (JCZ3)⁶ EoS. The fact that these EoS depend on parameters whose values are calibrated from experimental data has led to several reparametrizations of the same EoS, e.g., BKW-C⁵, BKW-S⁹, BKW-RR¹³, JCZS⁹, and JCZ3-J³.

Other models are eminently empirical in that they use equations that reflect phenomenological factors observed in testing. Thus, for instance, it has been experimentally observed that, within a range of densities, detonation velocity varies approximately linearly with explosive density. Empirical models include predictor variables other than density, such as detonation heat,

obtained once a product formation hierarchy has been established a priori. Use of empirical models is widespread, but especially widely employed¹⁸ is the Kamlet and Jacobs (KJ) model⁸ both for its simplicity and accessibility – properties not shared by the thermochemical models, which require the use of generally proprietary complex codes.

Bastante et al.⁴ compared the prediction capacity of different models, both experimental and thermochemical EoS-based. To evaluate model goodness-of-fit, relative residual (RR) statistics were used, defined as follows: $RR_i = (M_i - E_i)/E_i$ where M_i corresponds to the calculated values (D and P) and where E_i corresponds to the measured experimental values. Used as an indicator of residual dispersion was the root mean square residual (RMSR). One of the conclusions of Bastante et al.⁴ was that the Xiong¹⁷ experimental model is a better predictor of detonation velocity than the KJ model. Note, however, that the Xiong model uses far more prediction parameters and is also more complex to implement.

Another issue pointed out in Bastante et al.⁴ is that it is possible, using the IDT, to calculate detonation pressure if the analytical expression for detonation velocity is known. Experimental models have not taken this circumstance into account, so their predictive equations for D and P are not compatible with the IDT.

Starting from the premise that a model should be as simple as possible and should be compatible with the IDT, we developed a new predictive model from a first-order approximation of explosive detonation velocity. The proposed model proved to be as

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[†] Electronic Supplementary Information (ESI) available: The supplementary materials contain details of the experimental data and calculations and the results supporting our conclusions. A spreadsheet for the new predictive model is available.

simple as the KJ model to implement and was an excellent predictor of the main features that define the explosive performance of high explosives, that is, detonation velocity and pressure¹⁹.

The following sections describe the development of the model, the methodology used for calibration, the results and their analysis, and finally, our conclusions.

2 Model development

Let $C_aH_bN_cO_d$ be an explosive composition of density ρ_o , whose products in the detonation state release energy Q . According to the IDT²⁰, from $D = D(\rho_o, Q)$, an expression that can be approximated by the first-order Taylor series, we obtain:

$$D(\rho_o, Q) \cong D_o + \rho_o \frac{\partial D}{\partial \rho_o}, \text{ where } D_o = D(\rho_o \approx 0, Q = Q) \quad (1)$$

The first term on the right-hand side of Equation 1 can be estimated from equations obtained from the IDT applied to ideal gases:

$$D_o \cong \sqrt{2Q(\gamma_o^2 - 1)} \quad (2)$$

where, γ_o is, for the gaseous products, the ratio between specific heat at constant pressure and specific heat at constant volume. While γ_o depends on the temperature T of the detonation products, its value is not very sensitive to variations in T . The value of Q can be estimated from the difference between the standard formation enthalpies of reactants and products, assuming the latter is known.

The experimental predictive models simplify the determination of products using certain product formation hierarchies. Bastante et al.⁴ analysed the predictive capacity of several models, finding that the Xiong¹⁷ model obtained the best results in predicting detonation velocity in terms of minimizing the RMSR. Xiong proposed five hierarchies, applying one or another depending on the composition of the explosive. Thus, for a given composition, up to six of the eight products considered by Xiong may appear: H_2O , CO_2 , CO , CH_4 , O_2 , H_2 , N_2 , and $C(s)$ (Table 1).

Table 1 Decomposition of $C_aH_bN_cO_d$ explosive according to Xiong¹⁷, who proposes choosing a hierarchy according to explosive composition

Type—Oxygen Balance	Condition	Products
1 – rich or zero	$d - b/2 - 2a \geq 0$	H_2O, CO_2, N_2, O_2
2 – slightly deficient	$d - b/2 - 2a < 0$	$H_2O, CO_2, CO, CH_4, N_2, C$
3 – deficient	$d - b/2 - a \leq 0$	$H_2O, CO_2, CO, CH_4, N_2, C$
4 – seriously deficient	$d - b/2 < 0$ and $a \geq d$	$H_2O, CO, CH_4, H_2, N_2, C$
5 – seriously deficient	$d - b/2 < 0$ and $a < d$	H_2O, CO, H_2, N_2

The issue is that Xiong uses far more parameters than other empirical models, e.g., the KJ model considers only five products in its hierarchy, following a simple order of precedence: N_2 , H_2O , CO_2 , and O_2 or $C(s)$. For this reason, in constructing our model, we considered whether the use of complex hierarchies could be justified, as they require a large number of parameters to establish product composition depending on the explosive composition.

Experimentally, however, it was observed that, within a certain range of densities, the relationship between D and ρ_o is approximately linear. Thus, from Equation 1 it follows that the value of

$\frac{\partial D}{\partial \rho_o}$ should be approximately constant depending on the explosive.

The hypothesis used in developing our model is that said dependency can be expressed as a linear combination of the products established by the hierarchy:

$$\frac{\partial D}{\partial \rho_o} \cong \sum n_i c_i = w \quad (3)$$

where n_i represents the number of moles of product i per gramme of products, and c_i represents the value of a dependent parameter of product i . The c_i value is obtained by calibrating the model using experimental data.

From Equations 1 and 3:

$$D = D_o + w\rho_o \quad (4)$$

Equation 4 can be interpreted as a generalization of the Xiong¹⁷ model, according to which D is equal to:

$$D = 1.045Q^{\frac{1}{2}} + 404w_x\rho_o; D, Q, \rho_o \text{ and } w_x \text{ expressed in the IS of Units} \quad (5)$$

where w_x is the sum of detonation product co-volumes expressed in cubic meter per kilogram of explosive. In calculating w_x , Xiong¹⁷ introduces corrective multiplicative factors for certain explosive compositions, e.g., if the composition does not contain carbon, the value of w_x is multiplied by 1.25, if it does not contain hydrogen it is multiplied by 1.06, etc. Independently of the explosive, comparing the first term on the righthand side of Equation 5 with Equation 2, it follows that the Xiong model assumes a constant value of $\gamma_o = 1.24$.

Knowing the function $D(\rho_o, Q)$, detonation pressure can be calculated by applying the IDT. In the detonation state, the IDT²⁰ is fulfilled:

$$P = \frac{\rho_o D^2}{\gamma + 1} \quad \text{with } \gamma = \left(\frac{\partial \ln P}{\partial \ln \rho} \right)_s \quad (6)$$

$$\gamma = a + [(1+a)^2 + b]^{1/2} \text{ with } a = \rho_o/D(\partial D/\partial \rho_o) \text{ and } b = D(\partial D/\partial Q) \quad (7)$$

The values a and b are obtained by deriving Equation 4 and, once entered in Equation 7, we have the following expression:

$$\gamma = \frac{w\rho_o}{D} + \left[\left(1 + \frac{w\rho_o}{D} \right)^2 + \frac{DD_o}{2Q} \right]^{1/2} \quad (8)$$

Equation 8 shows, as might be expected, a value of adiabatic gamma γ that increases with the density value and some small dependence on Q (i.e., explosive composition). Since $D(\rho_o, Q)$ is known, introducing the calculated value of γ in Equation 6 yields a value for detonation pressure.

In summary, the proposed model obtains detonation pressure from the function $D(\rho_o, Q)$ by applying the IDT. In Xiong¹⁷, however, the isentropic expansion coefficient γ is calculated by an experimentally determined function that depends on explosive density and detonation product composition, for which reason the model is not compatible with the IDT.

From the above, for the proposed model it is clear that we need to define: (i) one or more product formation hierarchies, and (ii) either an average of γ_o independent of the product composition, or the temperature T to be used to calculate γ_o as obtained from the product composition resulting from the hierarchy selected in (i).

3 Model calibration method

The objective of model calibration was to determine both the definitive hierarchy to be used and the set of parameters Θ corresponding to that hierarchy, namely: (i) the coefficients c_i from Equation 3, and (ii) either T at which the value of γ_o is to be calculated or the mean value of γ_o independent of the explosive. Figure 1 illustrates the model calibration process.

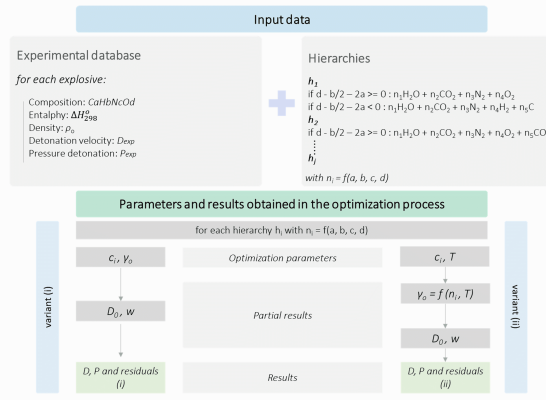


Fig. 1 Diagram illustrating model parameter calibration. For each hierarchy, the algorithm searches for the set of parameters (c_i and γ_o or T) that maximizes model likelihood: in (i) the value of γ_o is held constant, and in (ii) γ_o is obtained from T and the previously calculated composition of the products (n_i).

Our strategy was to calculate optimal Θ according to the maximum likelihood criterion, using, in the first instance, the simple KJ hierarchy: H_2O , CO_2 , N_2 , O_2 , C (including also the formation of H_2 in the event that there was not enough oxygen to oxidize all the hydrogen to H_2O). Other products in different proportions were subsequently incorporated into the hierarchy (e.g., CO at different CO/ CO_2 ratios), and the results were compared for all the hierarchies.

To limit the space of solution to Θ , the model was required to pass through a series of experimental points, in such a way that the modulus of the relative residual of the detonation velocity ($|RR_D|$) at each point was less than 1.6% (Table 2. This value is twice the standard deviation of the experimental error for detonation velocity measurements for Trinitrotoluene explosive (Bastante et al.⁴).

Note that the constraints in Table 2 largely define relationships between the coefficients c_i . For instance, for the decomposition of nitric oxide, as products we had 0.5 moles of O_2 and 0.5 moles of N_2 per mole of NO. Since the molecular mass of the products was 30 g/mol, the value of both $(n_i)_{O_2}$ and $(n_i)_{N_2}$ was 0.5/30. The value of Q was calculated as the difference between the standard

enthalpies of the formation of reactants and products, resulting in a value of 2.58 MJ/kg. For this example, the value of γ_o is taken as 1.24 (the value used by Xiong). Substituting the values of γ_o and Q in Equation 2, we obtain a value for D_o (1666m/s). Imposing the above constraint, we obtain:

$$(1 - 0.016) \times 5620 \leq \left[1666 + \frac{0.5}{30} \times (c_{O_2} + c_{N_2}) \times 1300 \right] \leq (1 + 0.016) \times 5620$$

Operating and rearranging terms we obtain:

$$178 \leq c_{O_2} + c_{N_2} \leq 186$$

Therefore, once one of the two coefficients has been defined, the variation margin for the other is quite narrow. Using the outlined procedure with the remaining constraints we find that the decomposition of hydrazoic acid defines the relationship between c_{N_2} and c_{H_2} , and that of cyanuric triazide, the relationship between c_{N_2} and c_C , and so on.

In calibrating the model, the criterion used was to maximize parameter likelihood using the log-likelihood function²³:

$$\ell \cong -\frac{1}{2} \left[\frac{RMSR_D^2}{s_D^2} + \frac{RMSR_P^2}{s_P^2} + \log \left(4\pi^2 s_D^2 s_P^2 \right) \right] \quad (9)$$

where the subscripts D and P refer to the detonation pressure, respectively. Thus, s_D^2 and s_P^2 represent the respective model error variances. Those two statistics, unknown a priori, are obtained in the process of maximizing the log-likelihood function.

The model was implemented in Python and resolved using the lmfit code²³. Note that, in calculating Q , +10 kcal/mol was used as the standard carbon formation enthalpy value¹⁷. This value is consistent with that reported by Ornellas²⁴ (+8.75 kcal/mol) "to account for the highly disordered form that carbon exhibits in detonation products".

The main conclusions obtained from analysing calibration results are as follows:

- The predictive capacity of the model using the KJ hierarchy is very high, as demonstrated below, with the imposed constraints amply satisfied, as shown in Table 2.
- Adding new products (CO, CH_4 , NO) to this hierarchy marginally improves predictions, although, from a statistical point of view, this improvement does not justify the inclusion of new parameters.
- Results from using the KJ hierarchy do not justify using a value of γ_o that varies with composition. Differences are insignificant in RMSR terms compared to using a fixed value of γ_o , not to mention that the calculation is easier.
- More complex hierarchies like those of Xiong¹⁷ slightly improve the results using a variable value for γ_o . This may be due to the fact that proportions are better approximated between the different gaseous products that determine the value of γ_o . Nonetheless, as already mentioned, the use of complex hierarchies that introduce more parameters does not appear to be justified.

Table 2 Model constraints ($|RR_D| < 1.6\%$), products (KJ hierarchy) and detonation velocity residuals for the final model

Explosive/composition	ρ_0 (g/cc) / D(m/s) [ref]	Type	Products (mol) H ₂ O/ CO ₂ / O ₂ / H ₂ / N ₂ / C	$ RR_D $
Nitric oxide/NO	1.30/5620 ²	1	0/0/0.5/0/0.5/0	-0.1%
Nitroglycerine/C ₃ H ₅ N ₃ O ₉	1.60/7700 ²	1	2.5/3/0.25/0/1.5/0	0.8%
Pentaerythritol tetranitrate/C ₅ H ₈ N ₄ O ₁₂	1.67/7980 ²	2	4/4/0/0/2/1	0.1%
Trinitrotoluene/C ₇ H ₅ N ₃ O ₆	1.64/6950 ²	3	2.5/1.75/0/0/1.5/5.25	-0.3%
Hexogen/C ₃ H ₆ N ₆ O ₆	1.80/8754 ²	3	3/1.5/0/0/3/1.5	-0.3%
Cyanuric triazide/C ₃ N ₁₂	1.50/7300 ²¹	4	0/0/0/0/6/3	0.4%
Hydrazoic acid/HN ₃	1.13/7570 ²²	4	0/0/0/0.5/1.5/0	-1.0%
Nitroguanidine/CH ₄ N ₄ O ₂	1.63/7980 ²	5	2/0/0/0/2/1	0.0%

Table 3 Proposed model parameter values obtained after optimization (KJ hierarchy)

γ_0	$w = \sum n_i c_i$					
	C _{H₂O}	C _{CO₂}	C _{O₂}	C _{H₂}	C _{N₂}	C _C
1.23	75	123	72	43	112	18

- The proposed model, using the KJ hierarchy and a fixed value of γ_0 , shows systematic bias in predicting detonation velocity for the C_aN_cO_d compositions, with a , c , and d greater than zero. To correct this problem, the value of w was increased by a small percentage (7%).

We also analysed the influence of the standard carbon formation enthalpy value on the model results. Oxygen-deficient explosives (types 3 and 4) give an optimal Θ , in which the enthalpy value is approximately +18 kcal/mol, while explosives with a slightly negative oxygen balance (type 2) give another optimal solution with an enthalpy value of zero. This is possibly due to the fact that the KJ hierarchy overestimates Q , although this overestimate is offset, at least in part, by the positive carbon enthalpy value. In statistical terms, we found small differences in the overall results between one and another value, which is why the initial value of +10 kcal/mol was maintained.

The optimal parameter values obtained after calibration are shown in Table 3, where it can be seen that our value of γ_0 is slightly lower than that of Xiong¹⁷.

4 Results and model goodness-of-fit

The analysis was carried out in the first instance by comparing the goodness-of-fit of our model (labelled DEoS) with that obtained for the other predictive models, using different experimental databases. Table 4 describes the number of explosives and experimental data included in each database and the compared models.

The first database was obtained from Pepekina and Gubin¹⁶, who propose BKW-RR parameterization of the BKW EoS. Table 5 in their article shows, for 48 single explosives, values for experimental velocity and velocity calculated using BKW-RR at densities close to their maximum value. The 48 explosives, representative of the five types defined by Xiong¹⁷, are composed exclusively of C, H, N, and O. This database is also used in Baker et al.³ where the velocity predictions are calculated using the Jaguar (JCZ3-J) parameterization of the JCZ3 EoS.

Using these data, the residuals of the different models were analysed. Figure 2 shows their distributions in the form of boxplots. The boxes show the dataset quartiles, while whisker exten-

sions indicate distribution ranges. Values not included in whiskers indicate outlier residuals for some explosive compositions; these values may be due either to the presence of an outlier in the database itself or to the fact that the model is not a good predictor for some compositions. In general, a smaller/larger whisker extension and the absence/presence of outliers is an indicator of greater/lesser reliability of the model.

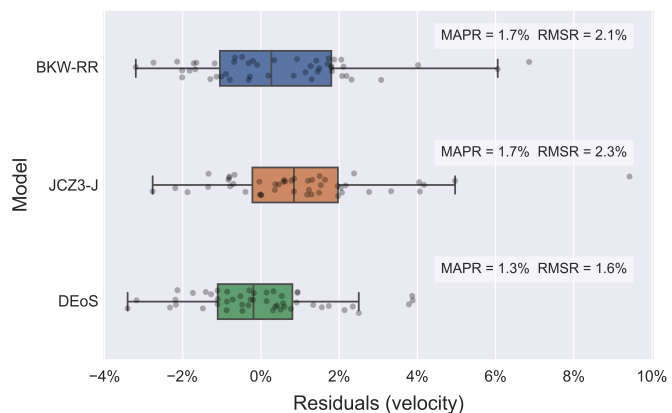


Fig. 2 Boxplot of velocity residuals (48 observations) using the BKW-RR, JCZ3-J and DEoS models.

Figure 2 shows that the DEoS predictions were excellent, with less bias, range and residual dispersion than the other two models, as corroborated and quantified by the RMSR and mean absolute percentage residual (MAPR) values. In our DEoS model, the mean of the residuals is practically zero, and the range and outlier values are significantly lower than those for the other two models.

The second database we used – obtained from McGee et al.¹, a study describing JCZS parameterization of the JCZ3 EoS – was substantially different from the above database⁵ (just two data items in common), and contained significantly more experimental data: $n=126$ observations for velocity and $n=86$ observations for pressure for 71 (25 single and 46 composite) explosives. Practically all the data were used (Tables 3 and 8 in McGee et al.'s paper¹), except for data on explosives with low densities (<1 g/cc) and explosives with a relatively high percentage ($>10\%$) of elements other than C, H, N, and O in their composition. In calculations for the DEoS model, these elements were considered to be inert, making their contribution to the calculation of the parameter w negligible.

Figure 3, showing boxplots for the JCZS and DEoS models, depicts the MAPR, RMSR values of the velocity and pressure resid-

Table 4 Databases used to analyse prediction goodness-of-fit

Database	No. of single/composite explosives	No. of experimental data D/P	Compared predictive models
First	48/-	48/-	BKW-RR, JCZ3-J, DEoS
Second	25/46	126/86	JCZS, DEoS
Third	75/163	519/263	KJ, DEoS

uals and also the 97.5 percentile (P97.5) values, indicative of the range of the residuals, and therefore, of model reliability. Velocity residuals are similar in both models, although the DEoS model had fewer outliers, indicating less dispersion and a smaller range. The JCZS model tended to underestimate the pressure experimental values (mean residual value -4.7% for JCZS and -0.6% for DEoS) and also showed greater dispersion (RMSR 7.9% for JZCS and 6.2% for DEoS).

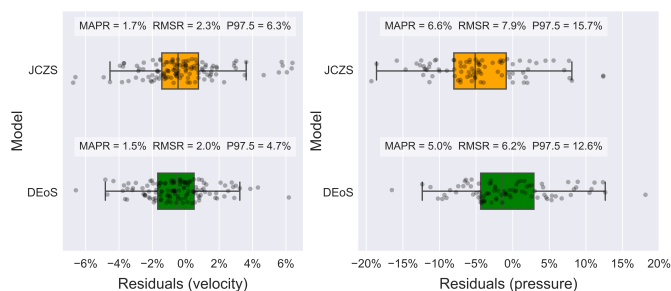


Fig. 3 Boxplots of velocity residuals (n=126 observations) and pressure residuals (n=86 observations) for the JCZS and DEoS models.

Therefore, despite including results for explosive compositions containing elements other than CHNO ($\approx 20\%$ of the database), the predictive capacity of the DEoS model was excellent, and especially bearing in mind that the JCZS model offers better predictions than other thermochemical models¹⁴.

To be able to conduct a more detailed analysis, a third database was created with a large number of observations and a wide range of explosive compositions (please see electronic supplementary information (ESI) for details †). This larger database was composed of n=519 and n=263 velocity and pressure observations, respectively, for 238 (75 single and 163 composite) explosives. The main characteristics of the explosives in this database are summarized in Table 5. Approximately 14% of the compositions contain percentages of Cl, F, P or Si.

Table 5 Composition and oxygen balance ranges of the analysed explosives

	Range (weight %)
[C]	0 / 43
[H]	0 / 10
[N]	13 / 98
[O]	0 / 65
[Cl/F/P/Si]	0 / 13
Oxygen balance	-99 / +53

Predicted velocity and pressure values were calculated using the DEoS and KJ models, and residuals were analysed. Since the KJ model only included compositions exclusively made up of C, H, N, and/or O, it included a smaller set of experimental data.

Figure 4 summarizes, for the KJ and DEoS models, the distribution functions for the modulus of detonation velocity and pressure residuals and the main statistical values. It clearly shows that the DEoS model's prediction capacity for velocity was excellent, surpassing that of the KJ model. The KJ showed a dispersion of the residuals twice that of the DEoS model, as well as a significantly greater range of residuals. As for pressure, the DEoS model results were also significantly better, especially in terms of the extension of the residual values, although less so than for velocity.

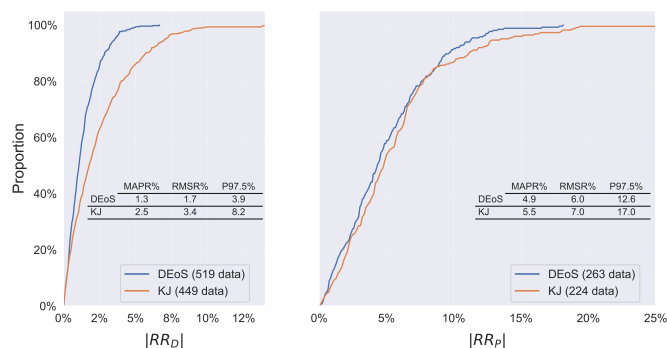


Fig. 4 Modulus distributions of velocity residuals and pressure residuals for the KJ and DEoS models.

Note that the dispersion of velocity residuals for the DEoS model when applied only to CHNO explosives was significantly lower (RMSR=1.6%) than when applied to explosives containing other elements (Cl, F, P or Si) in their composition (RMSR=2.2%). The influence of composition on results for the pressure residuals was minor.

Figure 5 shows boxplots of residuals broken down according to the types defined by Xiong¹⁷ (see Table 1). Given the scarcity of the corresponding experimental data, and since the analysis only included CHNO explosives, types 4 and 5 were grouped together. The DEoS model showed better residual behaviour than the KJ model for practically all explosive types, most especially for velocity, with residuals more centred around zero, less dispersion and smaller range. Note that there were only n=6 observations for pressure residuals for types 4 and 5.

To determine possible biases introduced by the predictor model, any analysis should include possible correlations between residuals and between model variables. From Figure 5 it can be inferred that the KJ model tended to overestimate velocity for the compositions richer in oxygen (types 1 and 2) and underestimate velocity for types 4 and 5.

This is corroborated by the evidence in Table 6, which shows the variables for which correlation with residuals had Pearson correlation coefficients (r) greater than 0.5. It can be deduced, from its high correlation values, that the KJ model had a tendency to overestimate the velocity of explosives with higher Q and higher

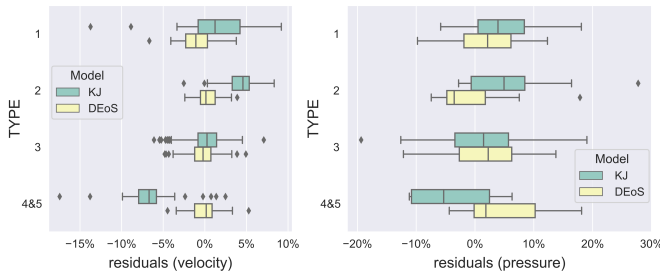


Fig. 5 Boxplots of velocity and pressure residuals for the KJ and DEoS models according to Xiong's¹⁷ types.

oxygen content in their composition, and to underestimate the pressure of explosives with greater brisance. This would suggest that it is not appropriate to compare, for example, KJ-predicted velocity for two explosives with significantly different oxygen content. Correlation values for the DEoS model, in contrast, were very low.

Table 6 KJ and DEoS model variables showing correlation coefficients (r) for velocity and pressure residuals

	KJ	DEoS
	RR_D	
Q	0.58	-0.11
%N	-0.63	0.02
%O	0.76	0.04
	RR_P	
γ_o	-0.51	-0.03
$\rho_{experimental}$	-0.59	-0.26

Having verified model goodness-of-fit in predicting velocity and pressure, the next step was to check the goodness-of-fit of predictions for other parameters derived from the IDT. The correlation coefficient for γ , as obtained from the experimental data and Equation 6 and as predicted by the DEoS model (Equation 8), was $r=0.53$ (RMSR=7%). It must be remembered that, given the uncertainty of the experimental values for velocity and pressure, we cannot expect high correlations between those other parameters, irrespective of the predictive model used. For instance, correlation for the KJ model was $r=0.44$.

Correlation between the density of the products in the detonation state (ρ_{c_j}) as obtained from the experimental data and from the DEoS model was also calculated. The value of ρ_{c_j} was derived from the IDT:

$$\rho_{c_j} \cong \frac{(\gamma+1)}{\gamma} \rho_o \quad (10)$$

The correlation between those parameters was very high ($r=0.99$, RMRS=1.9%); this was not the case for values of γ , attributable to the fact that ρ_{c_j} values are not very sensitive to variations in γ .

Some verifications were also performed on the value of other parameters of interest in the IDT. For instance, Wood and Fickett²⁵ indicated that "Typical changes in velocity are the order of one m/s for each cal/g change in the initial energy". For the DEoS model, the calculated mean value of $\frac{\partial D}{\partial \rho_o}$ was 1.0 m/s per cal/g.

Finally calculated were the values of the Jones (α) and the Grüneisen (Γ) parameters of the explosives contained in the

largest of the databases used. According to the IDT, in the detonation state these parameters can be expressed as:

$$\alpha = p \left(\frac{\partial v}{\partial E} \right)_p = \frac{1+\gamma}{1+a} - 2 \quad (11)$$

$$\Gamma = v \left(\frac{\partial p}{\partial E} \right)_p = \frac{\alpha \gamma}{1+\alpha} \quad (12)$$

where v and E are the volume and specific energy of the detonation products, respectively.

Since no experimental measurements for these parameters were available, approximate values as usually taken for them were used: $\gamma \approx 0.25$ and $\Gamma \approx 0.6 - 0.7$. These were compared with mean values obtained from the DEoS model, which, at 0.27 ± 0.02 for γ and 0.60 ± 0.6 for Γ , were consistent with the approximate values. As both those parameters depend on the partial derivatives of the EoS, this result, in our opinion, additionally supports the reliability of the DEoS model. Given the simplification regarding product composition, however, guarantees cannot be offered regarding all explosive compositions.

5 Conclusions

We developed a predictive model (DEoS) of the main features that define the explosive performance of high explosives, namely, detonation velocity and pressure. Used as an EoS was a first-order approximation of velocity, while pressure was obtained by applying the IDT to the EoS. The parameters for the DEoS model were calibrated from experimental data following the criterion of maximizing model likelihood.

While different variants of the DEoS model were analysed, finally selected was the simplest model, which used the KJ hierarchy to establish the reaction products – with, if necessary, hydrogen incorporated in very oxygen-deficient explosive compositions. Although prediction goodness-of-fit could be improved by introducing more complex hierarchies, on the basis of the available experimental data, such an improvement would not justify the increased number of parameters and the additional complexity of the model.

The goodness-of-fit of the DEoS model was verified by comparisons with other models using different experimental databases. Our results indicate that the DEoS model is less biased and shows less dispersion and a smaller range of residuals than more complex thermochemical models based on EoS.

In comparing the results of the DEoS and KJ models using a large database of 238 explosive substances, the predictive capacity for velocity and pressure of the DEoS model was superior to that of the KJ model. In an analysis broken down by explosive types, satisfactory results for bias and dispersion further confirmed the reliability of the DEoS model. Some doubt remains, however, about the reliability of pressure predictions for explosives very deficient in oxygen for which the availability of experimental data was reduced.

Since, unlike the KJ model, the DEoS model does not show correlation between the residuals and the predictor variables, it does not introduce systematic bias when predictions for different types of explosives are compared.

The DEoS model was also applied to explosive compositions containing up to approximately 10% Cl, F, P and/or Si. Although results were not as good as those obtained for the CHNO-type compositions, predictions were still satisfactory.

Finally calculated were DEoS model predictions for certain parameters dependent on partial derivatives of the EoS in the detonation state, namely, adiabatic gamma, detonation product densities, and the Jones and Grüneisen parameters, with the results indicating that the model was reasonably successful in predicting values for these parameters.

In short, our predictive model, based on both detonation theory and experimental results, is easily implemented and offers excellent predictive capacity for a wide range of explosive compositions.

Conflicts of interest

There are no conflicts to declare.

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