CONTENT

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Accuracy of prediction of explosives performance using an analytic equation of state for EXP-6 potential fluid

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Abstract

Explosive materials undergo rapid chemical reactions, followed by the release of (mostly) gaseous products and heat energy. The performance of an explosive is most often quantified in terms of released heat energy, detonation velocity, volume of released gases, and pressure generated. The possibility to accurately predict these parameters is essential for designing more efficient explosives.
In this paper, it is shown that using the analytic equation of state for EXP-6 potential fluid, incorporated into the thermochemical code EXPLO5, the detonation velocities and pressures of ideal explosives can be predicted with a maximum error comparable to the measurement errors.

Keywords: *explosives, detonation, thermochemical calculation, EXP-6 EOS, EXPLO5 code*

1. Introduction

The explosives community is constantly searching for more efficient and safer explosives for military and commercial applications. Traditional methods of developing new explosives and explosive formulations typically require extensive experimental work involving material synthesis and testing, which is time-consuming, resource-intensive, and associated with considerable safety risk [1,2].

With the development of computers and efficient numerical methods, theoretical prediction of explosive performance plays an increasingly important role and is now an indispensable part of the development process. Numerical modeling has revolutionized the way researchers approach the development of new explosives, enabling a significant reduction in research time, resources, and costs, compared to the traditional approach. Today, several methodologies are used to theoretically predict explosive properties and performance. Thanks to them, researchers can explore a large number of potential explosives and predict their properties and performance even before they are synthesized. In this way, it is possible to identify promising explosives much more quickly and focus on them in further laboratory testing.

For example, computational thermodynamics (quantum chemistry and molecular dynamics) can be used to calculate the thermodynamic properties of potential explosive molecules and to provide detailed insights into their molecular structure and behavior. Such calculation can provide the enthalpy of formation [3,4] and density [5], which are input parameters for thermochemical codes used for the calculation of detonation parameters.

Hydrodynamic codes (such as LS-Dyna, Autodyn, etc.) can be used to model the fluid hydrodynamics associated with the detonation of explosives. It includes modeling the shockwave propagation, initiation and propagation of detonation, expansion of gaseous products, and the response of surrounding materials to the explosion [6,7]. This calculation provides information about the effects of explosives under specified conditions, which facilitates the design of more efficient systems for military and industrial applications.

Thermochemical equilibrium codes solve thermodynamic equations between detonation products to find the chemical equilibrium at specified volume, pressure, and temperature [8]. When coupled with the Chapman-Jouguet (C-J) detonation theory, they can predict detonation parameters such as detonation velocity, detonation pressure, heat, composition and concentration of detonation products, etc. [8, 9]. The first thermochemical codes appeared about 70 years ago (the RUBY code, Lawrence Radiation Laboratory, USA), and the BKW code (Los Alamos Scientific Laboratory, USA). In the 1960's, Stanford Research Institute developed the TIGER code. In 1994, Lawrence Livermore Laboratory converted the TIGER code to the CHEETAH code [10]. At the beginning of the 21st century, a few more codes appeared: TDS [11], EXPLO5 [9], CARTE [12] and others.

The mentioned codes are based on the Chapman-Jouguet detonation theory of detonation [13,14], with CHEETAH and EXPLO5 having also a built-in Wood-Kirkwood detonation model [15] that allows the calculation of detonation parameters for non-ideal explosives. The key difference between the codes is in the equations of state they use to describe the state of gaseous and condensed

products under conditions of extremely high pressure and temperature.

In addition to thermochemical codes, simpler empirical equations are often used to predict certain detonation parameters. These equations correlate various physical and chemical properties of explosives with their performance parameters such as detonation velocity, pressure, and energy output [1, 2, 16, 17, 18]. An excellent review of empirical equations and their accuracy is given in the paper by Muravyev et al. [1]

Machine learning and artificial intelligence have recently become increasingly relevant in the theoretical prediction of explosive performance [19, 20]. These emerging fields have the potential to significantly contribute to the improvement of the accuracy of performance prediction of potential explosives.

Although thermochemical equilibrium codes have been in use for several decades and are an indispensable tool in predicting the output of detonation, there are still challenges related to improving the accuracy of prediction. This paper deals with the accuracy of the prediction of key detonation parameters using an analytic equation of state for EXP-6 potential fluid, incorporated into thermochemical code EXPLO5, with an emphasis on the influence of some input parameters on the accuracy.

2. Description of detonation model

Upon initiation explosives undergo a series of rapid chemical reactions, producing (mainly) gaseous products and thermal energy. Explosive reactions are self-sustaining and propagate layer-by-layer through the explosives. Depending on the way of initiation and characteristics of the explosive, they may propagate at subsonic (e.g., combustion and deflagration) or supersonic velocities (detonation). Unlike combustion, detonation produces a shock wave that travels at a speed approaching 10 km/s, reaching 50 GPa pressure, and 6000 K temperature in nanoseconds [8]. Due to such extreme conditions, the energy transport from reacted to the unreacted layer of explosive by heat conduction, viscosity, and radiation is negligibly small compared to energy transport by motion (shock wave). Under such pressure the strength of any explosive material is negligible, and it responds hydrodynamically. The detonation process may be described by the Chapman-Jouguet (C-J) and Zeldovich-von Neumann-Doring (ZND) hydrodynamic detonation theories based on the conservation of mass, momentum, and energy across a jump-wise transition from unreacted to a reacted state of explosive [13,14].

The transformation of CHNO explosives into detonation products may be described by the following generalized formula:

$$C_cH_hN_nO_o \rightarrow n_1H_2O + n_2H_2 + n_3O_2 + n_4CO_2 + n_5CO + n_6CH_4 + n_7NH_3 + n_8N_2 + n_9NO + n_{10}C + \ldots$$

where n_1 - n_N are the mol amount of individual products. The transformation occurs very fast (on a nanosecond or microsecond scale, depending on the properties of the explosive). The C-J detonation model, incorporated in EXPLO5 code, assumes explosives transform into products instantly, so kinetics of reactions does not play a role. The heat generated in the reactions heats the detonation products to several thousand degrees, resulting in the generation of pressure of several tenths of GPa. In conditions of such high temperature and pressure, the detonation products represent a reactive system in which rapid reactions between individual products take place. As a result, the state of thermochemical equilibrium establishes very rapidly, resulting in no change in the concentration of products over time. The equilibrium concentration (i.e., mole numbers) of individual detonation products can be calculated by minimising the Gibbs free energy, preserving simultaneously the mass balance principle [21,22]. For a mixture of detonation products consisting of N different chemical species being in M different phase states, Gibbs free energy (G) is a function of temperature, pressure, and mole number of each product in each phase (n_i^k) [21]:

$$G = \sum_{k=1}^{M} \sum_{i=1}^{N} n_i^k \mu_i^k \quad (1)$$

where n_i^k is the number of moles of product i in phase k, and μ_i^k is the chemical potential of product i in phase k

To determine the equilibrium composition of detonation products by minimising the Gibbs free energy, EXPLO5 uses a method developed by White et al. [22] and adapted for computer application by Mader [13]. The method involves forming and solving a system of nonlinear equations, derived from the established thermodynamic relationships, in which the concentrations of individual products (n_i^k) are unknown. The calculation gives the product concentration and the thermodynamic functions at a specified volume (or pressure) and temperature. By combining this calculation with the C-J detonation theory, detonation parameters such as detonation velocity, pressure, heat, temperature, etc., can be derived.

EXPLO5 determines the C-J point as a point on the shock adiabat of detonation products at which the detonation velocity, calculated by Eq. 2, has its minimum value [13]:

$$D = V_0 \sqrt{\frac{p - p_0}{V_0 - V}} \quad (2)$$

where D is the detonation velocity, p_0 and V_0 are the initial pressure and volume of the explosive, p and V are the pressure and volume of products on the shock adiabat of products. To find the minimum of D, i.e., the C-J point, a minimisation algorithm is employed. Once the C-J point is determined, the detonation parameters are derived using the relationships that follow from the C-J theory.

An integral part of the EXPLO5 code is an extensive database of explosives and ingredients of explosive mixtures (containing explosive formulas, densities, and enthalpies of formation), and a database of products containing three sets of information: a) formula, enthalpy of formation, and density, b) polynomial constants describing the dependence of standard thermodynamic functions on temperature, and c) constants in the equations of state of gaseous and condensed detonation products.

Equations of state of gaseous and condensed products

The C-J detonation model is supplemented by equations of state (EOS) capable of describing accurately the thermodynamic behaviour of condensed and gaseous products in a very broad range of pressures and temperatures. Until about 20 years ago, all thermochemical codes used semi-empirical EOS (most often the Becker-Kistiakowsky-Wilson EOS, BKW), while more recently sophisticated theoretically based fluid EOS have been increasingly used [11,12,23]. Such an equation, named EXP-6, is incorporated in the EXPLO5 code [9, 24]. It is based on statistical mechanical theory and the Buckingham α-exponential-6 (EXP-6) model to describe the interaction energy between the product [8]:

$$u(r) = \frac{\varepsilon}{\alpha - 6}\left[6e^{\alpha(1-r/r_m)} - \alpha\left(\frac{r_m}{r}\right)^6\right] \quad \text{for } r > r_c \qquad (3)$$

$$u(r) = \infty \quad \text{for } r \le r_c$$

where $u(r)$ is the central pair potential; ε is the depth of attractive well between particles, r is separation distance, r_m is the position of the potential well minimum, α is the stiffness of the repulsive potential; first term in square brackets describes repulsive forces, second term attractive forces.

Direct implementation of Eq.3 in a thermochemical code would result in an unacceptably long calculation time, regardless of what statistical mechanical theory is applied. This drawback was successfully solved by Byers Brown [25] who proposed a method based on the analytical representation of the excess Helmholtz free energy (A^{ex}) in terms of transformed thermodynamic variables. According to the author, the excess Helmholtz free energy function ($F=A^{ex}/Nk_BT$) for the one-fluid mixture model (which assumes a mixture of products is a hypothetical one-component fluid with an effective EXP-6 potential) can be expressed as a function of three reduced variables; α, T*, and ρ* [25]:

$$F(\alpha, T^*, \rho^*) = \frac{A^{ex}(T,V,N;\, r_m,\varepsilon,\alpha)}{Nk_BT} \qquad (4)$$

where F is the excess free energy function, T* and ρ* are dimensionless temperature and density ($T^* = k_BT/\varepsilon$, $\rho^* = Nr_m^3/V$), respectively; k_B is the Boltzmann constant, N is the number of particles, and V is volume.

For the practical application of Eq. 4, Byers Brown proposed a three-variable (α,T^*,ρ^*) analytical representation of the excess free energy function $F(\alpha,T^*,\rho^*)$ using the Chebyshev polynomials. The author determined polynomial coefficients using $F(\alpha,T^*,\rho^*)$ values generated by applying the Weeks-Chandler-Anderson/Ree (WCA/Ree) hard-sphere perturbation theory [25]. Once $F(\alpha,T^*,\rho^*)$ is known, the excess Helmholtz free energy can be derived ($A^{ex}=F\cdot Nk_BT$). All other thermodynamic quantities can then be derived from A^{ex} [25, 26]:

$$p = -\left(\frac{\partial A(V,T)}{\partial V}\right)_T$$

$$S(V,T) = -\left(\frac{\partial A(V,T)}{\partial T}\right)_V \qquad (5)$$

$$\mu_i = \left(\frac{\partial A(V,T)}{\partial n_i}\right)_{V,T,\{n\}}$$

$$E(V,T) = A(V,T) + T \cdot S(V,T)$$

Eq. 4 represents a trivariate analytical representation of the thermodynamic equation of state based on EXP-6 potential [25]. EXPLO5 uses multinomial coefficients of order 4x4x4 (64 polynomial coefficients) to describe the $F(\alpha,T^*,\rho^*)$ function in α, T^*, ρ*domains of interest in detonation physics [9,24]. In addition to the multinomial coefficients, the interaction potential parameters (r_m, ε, α) for each gas phase detonation product must be known. The values of potential parameters for main detonation products are given in Table 1.

Table 1. The like-pair EXP-6 potential parameters for main detonation products

Product	$r_{m,ii}$ (Å)	ε_{ii}/k_B (K)	α_{ii}	λ_{ii}	Ref.
H_2O	3.25	188.0	13.3	496	[27]
H_2	3.49	30.4	11.2	0	[2]
O_2	3.83	121.2	13.6	0	[23]
CO_2	4.22	230.2	13.8	0	[29]
CO	4.16	105.5	13.2	0	[23]
N_2	4.13	101.0	13.1	0	(24)
CH_4	4.30	137.8	12.3	0	[23]
CH_2O_2	4.62	150.0	13.0	0	(24)
NH_3	3.95	96.7	12.9	117	[27]
NO_2	4.27	338.0	13.6	0	[23]
NO	3.71	151.9	13.1	0	[23]

For polar molecules, such are H_2O, NH_3, etc., EXPLO5 uses temperature-dependent well depth, as suggested by Ree [26]:

$$\varepsilon_{ii}(T) = \varepsilon_{0,ii}\left(1 + \frac{\lambda_{ii}}{T}\right) \qquad (6)$$

where λ_{ii} is constant (for non-polar molecules $\lambda_{ii} = 0$).

Under high pressures condensed detonation products are compressible and their compressibility is described by Murnaghan EOS [30]:

$$V = V_0[n\kappa P + \exp\{-\alpha_e(T - T_0\}]^{-\frac{1}{n}} \qquad (7)$$

where: V_0 is the molar volume when p=0 and T=T_0, T_0 is the temperature of the reference isotherm (298.15 K), κ is the inverse of the isothermal bulk modulus, α_e is the volumetric coefficient of thermal expansion, n is the constant.

Condensed carbon represents an important detonation product for some explosives. It is assumed in this paper that condensed carbon forms two solid phases (diamond and graphite) and two liquid phases (diamond-like and graphite-like liquid phases) [31], where the concentration of individual phases is determined by the phase equilibria at the given p, V, T conditions. The Murnaghan parameters for condensed carbon, used in this study, are given in Table 2.

Table 2. Parameters in Murnaghan EOS of condensed carbon

Phase	ΔH_f^o (kJ/mol)	V_0 (cm³/mol)	α_e, (m/mK)	κ_0, (1/bar)	n
Graphite	28.2	5.286	2.32E-05	2.32E-06	7.1
Diamond	21.1	3.64	2.43E-06	2.30E-07	2.4
Graphite-like liquid	81	6.00	2.32E-05	2.32E-06	7.1
Diamond-like liquide	125	3.95	2.43E-06	2.96E-07	2.4

Legend: Values of ΔH_f^o taken from Viktorov et al. [32], V_0 taken from Fried and Howard [31], and values of α_e, κ_0, and n taken from Suceska [9].

3. Experiment and discussion

To estimate the accuracy of prediction of detonation velocity (D) and detonation pressure (p_{CJ}) using the EXP-6 equation of state, a set of explosives for which reliable experimentally determined D and p_{CJ} exist was used. The set consists of several standard and well-characterised individual high explosives (RDX, HMX, TNT, PETN, NG, NM, TNM, Tetryl, etc.), four mixture-type of explosives (RX-23-AA, RX-23-BB, RX-23-CC, ANFO), and three explosives that exhibit non-ideal behaviour (ANFO, TATB, NQ). A total of 48 explosives of different compositions (CHNO, CNO, HNO, and NO) and densities (from 0.25 to 1.97 g/cm³) were analyzed (Table 3).

Model derivation

Input parameters for thermochemical calculation include parameters of explosives (formula, density, and enthalpy of formation) and parameters of detonation products (EOS of gaseous and condensed products and thermodynamic functions of the state as a function of temperature). The detonation parameters of studied explosives are calculated for the initial densities of explosives (ρ_0) at which the detonation velocities and pressures are measured. The enthalpies of formations are taken from the EXPLO5 database [9]. The EXP-6 potential parameters (r_m, ε/k_B, α) for the main detonation products used in the calculations are listed in Table 1, and the parameters in Murnaghan EOS of condensed carbon are given in Table 2. The thermodynamic functions of detonation products in their standard state are calculated from the enthalpy, where the dependence of enthalpy on temperature is expressed by a fourth-degree polynomial. The dependence of thermodynamic functions on temperature is taken from JANAF thermochemical tables [33].

Validation of model against experimental data

The detonation velocity is a detonation parameter that can be measured more accurately than other detonation parameters, with an accuracy of ±1 m/s [1]. However, some factors (such as variation in charge density, charge diameter, length, way of initiation, etc.) can significantly affect the measured value, which results in a variation of the experimentally determined velocity by a few percent [13]. The influence of the mentioned factors is much more pronounced in the case of explosives that exhibit non-ideal behavior, that is, a strong dependence of the detonation parameters on the size of the explosive charge. An analysis performed using experimental $D = f(\rho_0)$ data for RDX, HMX, and PETN, published in Hobbs and Baer [34], showed that the maximum difference between the measured detonation velocities and the velocities calculated from the best-fit equation varies from -176 m/s to 218 m/s (MAE=47 m/s, MAPE=0.69%). Chirat and Pittion-Rossillon [35] state that the results of individual authors differ by about 2 % (which corresponds to 60 m/s for D=3000 m/s and 180 m/s for D=9000 m/s).

Experimental determination of the detonation pressure is quite complex and involves different indirect and direct methods [36]. The measuring uncertainty is generally quite large. According to Hobbs and Baer [34] detonation pressures measured by various indirect methods range from 10 to 20 % (which corresponds to 3 to 6 GPa for p_{CJ}=30 GPa), while according to Chirat and Pittion-Rossillon [35] they range from 5 to 10 % (which corresponds to 1.5 to 3 GPa for p_{CJ}=30 GPa). Moreover, Kamlet and Dickinson [37] showed that analysis of the same raw experimental data by different research groups yields detonation pressures that differ up to 3.2 GPa. An analysis conducted in this work using experimental $p_{CJ} = f(\rho_0)$ data for RDX, HMX, and PETN, published in Hobbs and Baer [34], showed that the largest difference between the measured detonation pressures and the pressures calculated from the best-fit equation varies from -13.3 to 19.7 GPa (MAE=5.7 GPa, MAPE=2.7%)

A typical example of the output results of thermochemical calculations, for TNT and HMX, is given in Table 3. The calculated values of detonation velocities and pressures for all studied explosives are given in Table 4.

Table 3. The main calculation results for TNT and ANFO

	Parameter	Explosive name		
		TNT	TNT	HMX
Input parameters	Formula	$C_7H_5N_3O_6$	$C_7H_5N_3O_6$	$C_4H_8N_8O_8$
	ρ_0 (g/cm³)	1.64	1.00	1.90
	ΔH_f^o (kJ/mol)	-59.35	-59.35	74.79
Detonation parameters	Q_d (kJ/kg)	-4610.8	-3864.0	-5683.6
	T_d (K)	3279.2	3196.2	3290.0
	p_{CJ} (GPa)	18.56	6.92732	40.04
	D (m/s)	6793.5	5079.4	9186.2
	M_g (g/kg)	755.1	867.1	966.6
	M_c (g/kg)	244.9	132.9	33.4
	V_0 (dm³/kg)	561.9	728.6	673.9
Detonation products (mol/mol of explosive)	H_2O(g)	1.778923	1.170727	1.689581
	H_2(g)	0.021015	0.334555	0.00223
	N_2(g)	1.459389	1.420841	3.971715
	CO_2(g)	1.346396	0.753262	0.890896
	CO(g)	0.442643	3.088343	0.053333
	CH_2O_2	0.537068	0.105005	2.231501
	NH_3(g)	0.071140	0.096876	0.04740
	C(diamond)	3.696519	0	0.823152
	C(graphite)	0.934918	2.513321	0
	CH_4(g)	0.011813	0.203017	0.000188
	C_2H_4(g)	0.007504	0.11312	0.00008

Legend: ρ_0–initial density, ΔH_f^o– standard enthalpy of formation, Q_d – heat of detonation, T_d – detonation temperature, M_g and M_c – mass of gaseous and condensed products, V_0 – volume of gas at STP

Two important things can be observed from Table 2. First, the composition of detonation products for the same explosive changes with explosive density. For example, 1 mole of TNT having a density of 1.64 g/cm^3 produces 3.696 moles of carbon in the form of diamond and 0.935 moles in the form of graphite, while TNT with a density of 1.0 g/cm^3 produces only carbon in the form of graphite (2.51 moles). Second, detonation parameters (D, p_{CJ}, Q, T, etc.) for the same explosive change with the density of explosives D(at 1.64 g/cm^3)=6793.5 m/s, D(at 1.0 g/cm^3) =5079.4 g/cm^3).

Table 4. Experimental and predicted values of detonation velocities and pressures

Reactant names	Formula	ΔH_f^o (kJ/mol)	ρ_{TMD} (g/cm^3)	ρ_0 (g/cm^3)	$D_{expt.}$ (m/s)	$D_{calc.}$ (m/s)	Dif. (m/s)	p_{CJ_expt} (GPa)	p_{CJ_calc} (GPa)	Dif. (GPa)	Ref.
Octogen (HMX)	$C_4H_8N_8O_8$	74.80	1.905	1.89	9115	9143	27	39.00	39.25	0.25	[34
Octogen (HMX	$C_4H_8N_8O_8$	74.80	1.905	1.60	8040	7981	-59	28.00	26.52	-1.48	[34
Octogen (HMX)	$C_4H_8N_8O_8$	74.80	1.905	1.40	7300	7369	69	21.00	20.60	-0.40	[34
Octogen (HMX)	$C_4H_8N_8O_8$	74.80	1.905	1.20	6560	6700	140	15.70	14.34	-1.36	[34
Octogen (HMX)	$C_4H_8N_8O_8$	74.80	1.905	1.00	5805	5934	128	10.90	9.42	-1.48	[34
Octogen (HMX)	$C_4H_8N_8O_8$	74.80	1.905	0.75	4890	4923	32	6.10	5.13	-0.97	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	1.80	8754	8766	11	34.70	34.56	-0.14	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	1.60	8130	7995	-135	26.90	26.61	-0.29	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	1.40	7425	7387	-38	20.10	20.85	0.75	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	1.20	6541	6716	175	14.50	14.44	-0.06	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	1.00	5952	5949	-3	10.00	9.47	-0.53	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	0.70	4765	4739	-26	4.80	4.53	-0.27	[34
Hexogen (RDX)	$C_3H_6N_6O_6$	70.31	1.806	0.56	4165	4200	35	3.30	3.03	-0.27	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	1.763	8270	8394	124	31.00	30.43	-0.57	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	1.45	7180	7220	40	20.80	19.39	-1.41	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	1.23	6342	6365	23	14.50	12.89	-1.61	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	0.99	5475	5397	-78	8.60	7.69	-0.91	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	0.88	5077	4965	-112.	6.90	5.96	-0.94	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	0.48	3631	3551	-80	2.30	1.99	-0.31	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	0.30	2980	3016	36.	1.10	1.00	-0.10	[34
Pentrit (PETN)	$C_5H_8N_4O_{12}$	-533.65	1.78	0.25	2830	2879	49	0.80	0.79	-0.01	[34
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	-59.35	1.654	1.64	6942	6793	-149	18.90	18.56	-0.34	[34
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	-59.35	1.654	1.45	6494	6387	-107	14.60	14.55	-0.05	[34
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	-59.35	1.654	1.36	6207	6095	-112	12.50	12.78	0.28	[34
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	-59.35	1.654	1.00	5060	5079	19	6.80	6.93	0.13	[34
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	-59.35	1.654	0.80	4423	4493	70	4.60	4.43	-0.17	[34
Tetryl (CE)	$C_7H_5N_5O_8$	33.68	1.73	1.68	7500	7507	7	23.90	23.05	-0.85	[34]
Tetryl (CE)%	$C_7H_5N_5O_8$	33.68	1.73	1.614	7479	7281	-198	22.60	21.33	-1.27	[34
Nitroglycerine (NG)	$C_3H_5N_3O_9$	-370.79	1.60	1.60	7750	7665	-85	22.00	22.22	0.22	[40]
Nitromethane (NM)	CH_3NO_2	-113.09	1.16	1.13	6350	6331	-19.	12.00	12.68	0.68	[34]
Nitric oxide (NO)	NO	79.51	1.30	1.30	5620	5499	-121	10.00	9.47	-0.53	[41]
Tetranitromethane (TNM)	CN_4O_8	37.24	1.65	1.64	6360	6361	1	15.90	14.62	-1.28	[34]
Hexanitro-ethane (HNE)	$C_2N_6O_{12}$	85.00	1.86	1.86	7580	7471	-109	-	23.27	-	[41]
Hexanitro-benzene (HNB)	$C_6N_6O_{12}$	188.00	2.02	1.973	9384	9323	-61	39.00	39.32	0.32	[41]
Benzotris-furoxane (BTF)	$C_6N_6O_6$	602.50	1.90	1.86	8490	8554	64	35.10	31.35	**-3.75**	[34
Benzotris-furoxane (BTF)	$C_6N_6O_6$	602.50	1.90	1.76	8260	8184	-76	-	28.37	-	[34
Hexanitro-azobenzene (HNAB)	$C_{12}H_4N_8O_{12}$	284.00	1.80	1.60	7310	7254	-56	20.50	22.56	2.06	[34
Diamino-dinitro ethylene (FOX-7)	$C_2H_4N_4O_4$	-134.10	1.885	1.78	8325	8527	202	28.40	30.75	2.35	[34
Diamino-trinitro benzene (DATB)	$C_6H_5N_5O_6$	-117.81	1.84	1.78	7600	7651	51	25.10	22.81	-2.29	[34
Triamino-trinitro benzene (TATB)	$C_6H_6N_6O_6$	-154.00	1.94	1.85	7660	8123	**463**	25.90	26.04	0.14	[34
Triamino-trinitro benzene (TATB)	$C_6H_6N_6O_6$	-154.00	1.94	1.50	6760	6614	-146	17.50	17.21	-0.29	[34
Nitroguanidine (NQ)/ /Estane (95%/5%)	$C_{1.246}H_{4.29}N_{3.9}O_{2.039}$	-113.88	1.727	1.704	8280	8596	**316**	26.80	26.04	-0.76	[34
Nitroguanidine (NQ)	$CH_4N_4O_2$	-95.34	1.77	1.72	8346	8799	**453**	-	27.94	-	[34
Nitroguanidine (NQ)	$CH_4N_4O_2$	-95.34	1.77	1.55	7650	7806	156	-	20.78	-	[34
Ammonium nitrate/ Fuel oil (94/6)	$C_{0.361}H_{4.442}N_{1.928}O_{2.882}$	-351.08	1.624	0.84	4740	4670	-70	6.14	4.74	-1.40	[39]
RX-23-AA (79%HyN/21%Hy)	$H_{4.551}N_{2.551}O_{1.652}$	-115.30	1.424	1.424	8580	8547	-33	20.90	22.97	2.07	[40]
RX-23-AB (69%HyN/5%Hy/26%H_2O)	$H_{3.074}N_{1.074}O_{1.557}$	-247.98	1.384	1.384	7480	7506	26	18.60	16.51	-2.09	[40]
RX-23-AC (32%HyN/68%Hy)	$H_{4.139}N_{2.139}O_{0.418}$	9.90	1.136	1.136	7870	7679	-191	16.90	15.00	-1.90	[40]
						MAE	99.5 m/s		MAE	0.89 GPa	
						MAPE	1.46 %		MAPE	6.29 %	
						RMSE	139.1 m/s		RMSE	1.21 GPa	
							1.92 %			8.07 %	

Legend: ρ_{TMD}– theoretical maximum, $D_{expt.}$ and $D_{calc.}$- experimental and calculated detonation velocities, $p_{CJ\_expt.}$ and $p_{CJ\_calc.}$- experimental and calculated detonation velocities Dif. - the difference between experimental and calculated value, MAE – mean absolute error, MAPE – mean absolute percentage error, RMSE – root mean square error

Based on the analysis of the results given in Table 4 and Fig.1, it can be concluded that there is a good agreement between the calculated and experimental values of detonation velocities (R^2=0.9996 σ=139.3 m/s, and MAPE=1.46 %). The same is evident from Fig. 2, which shows the distribution of errors. For 40 explosives out of 48 studied (83.34 %), the difference between the calculated and experimental values is below 150 m/s, which is within the measurement error. For 45 explosives (93.76%) the error is below 250 m/s (which is a bit above maximum measurement error).

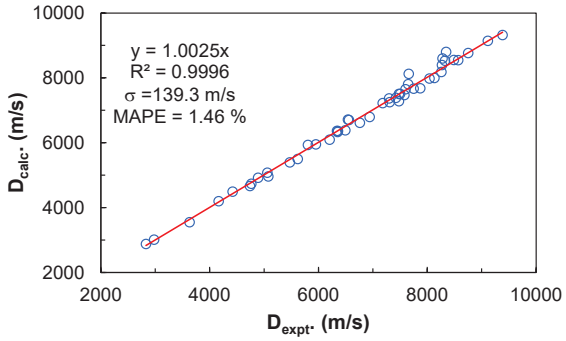

Fig. 1. Experimental *vs.* calculated detonation velocities for tested explosives

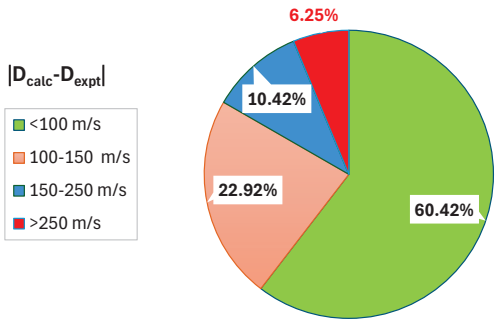

Fig. 2. Pie chart showing distribution of detonation velocity prediction errors

The difference between the measured and experimental values of detonation velocity is greater than 300 m/s (i.e. 5%) only for three explosives: TATB (+463 m/s), NQ (+453 m/s), and NQ/Estan (+316 m/s). All three explosives behave non-ideally [38], which means their detonation properties strongly depend on charge size [13]. The experimental data for NQ and TATB used in this study refer to infinite (i.e., ideal) detonation velocities, which means the value of D is obtained by extrapolating experimental D-1/d (where d is the charge diameter) dependence, obtained at smaller charge diameters, to an infinite diameter ($d \rightarrow \infty$). Extrapolating from smaller diameters to an infinite diameter may introduce an additional error, which may be the reason for the larger deviation between the calculated and experimental detonation velocities for the mentioned explosives. The following data also support the assumption that the experimental detonation velocities at infinite diameters for NQ and TATB are probably insufficiently accurate. Hobbs et al. [10] calculated detonation velocities of NQ and TATB using three different EOS and obtained significantly higher values of detonation velocities compared to the experimental (260 to 392 m/s for NQ and 469 to476 m/s for TATB) – which closely agrees with the results of this study. In addition, the calculated detonation velocity for highly non-ideal ANFO differs from the experimental infinite detonation velocity by only 70 m/s. This is most likely because the detonation velocity is measured using a huge explosive charge – about 109 tons [39], so that the diameter of the charge was close to infinity.

A comparison between the experimental and calculated values of detonation pressures is given in Figs. 3 and 4. Fig.3 shows that the calculated values are consistently a bit lower than the experimental (the slope of the line is 0.9807). For 38 explosives out of 44 tested (86.0%), the difference between the experimental and calculated pressures is less than 2 GPa, which is within the measurement error. However, MAPE is quite high (6.29%) because the error expressed in percentages is higher at lower pressures. For example, an error of 1 GPa at a pressure of 10 GPa gives a percentage error of 10%, while at a pressure of 35 GPa it gives a percentage error of 2.9%).

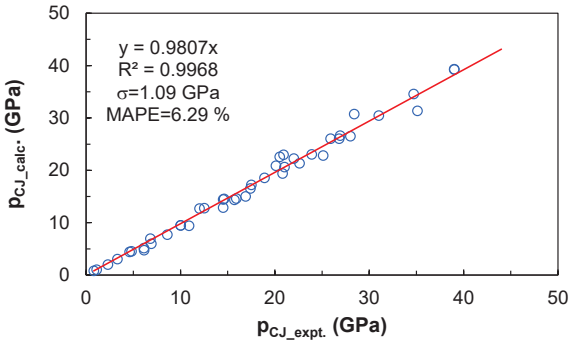

Fig. 3. Experimental *vs.* calculated detonation pressures for tested explosives

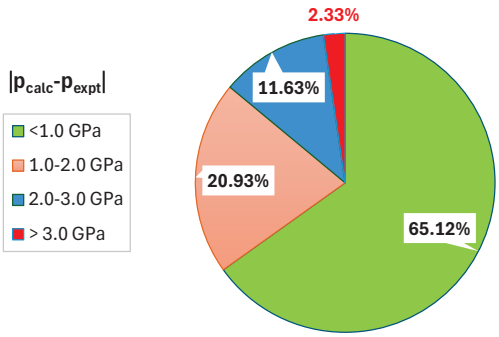

Fig. 4. Pie chart showing distribution of detonation pressure prediction errors

The difference between the measured and calculated detonation pressures is greater than 3 GPa only in the case of BTF (difference equals -3.75 GPa). Interestingly, BTF, whose detonation temperature is above 4200 K and pressure above 30 GPa, is the only one of the tested explosives to produce a diamond-like liquid carbon (other explosives produce either graphite or diamond). Thus, the larger error

in the case of BTF may be attributed to the deficiencies in the liquid carbon EOS.

Although there is not enough data for a reliable statistical analysis of the prediction errors of dCJ and pCJ for the different classes of explosives analyzed (only 6 data for non-ideal explosives and 3 data for the HNO mixture-type explosives), the analysis given in Table 5 shows that the prediction accuracy is higher for standard and well-characterized explosives than for other tested classes of explosives.

Table 5. Prediction accuracy for different classes of explosives

Explosive class	Data points*	Detonation velocity		Detonation pressure	
		MAE (m/s)	MAPE (%)	MAE (GPa)	MAPE (%)
All explosives	48/44	99.5	1.46	0.87	6.29
Standard	39/37	75.2	1.18	0.83	5.85
Non-ideal	6/4	267.5	3.50	0.65	6.96
Mixture-type (HNO)	3/3	79.7	1.01	2.02	10.79

Legend: * the first number refers to the number of experimental data for detonation velocity, second for detonation pressure

In the case of non-ideal explosives predicted detonation velocity is significantly overestimated (due to the reasons discussed previously), while in the case of HNO mixture-type explosives detonation pressure is largely overestimated. Given that HNO explosives produce a large amount of polar products, H_2O and NH_3, the reason for the discrepancy could be in an insufficiently accurate equation of state for NH_3 and H_2O (Eq. 6), especially at lower detonation temperatures.

Impact of input data on accuracy of prediction of detonation velocity and pressure

The accuracy of thermochemical calculation is influenced by the accuracy of input data on explosives (ρ_0, ΔH_f^0), the accuracy of EOS of the detonation products, and the accuracy of thermodynamic functions of the state of the detonation products. The thermodynamic state functions (*H, E, c_v, S, G*, μ, etc.) of the main detonation products, in the range 298–6000 K, are taken from the JANAF tables [33] and they are considered to be very accurate. As far as EOS gaseous detonation products are concerned, so far several authors have shown that EXP-6 EOS gives the most accurate results in a broad range of temperatures and densities [10, 11, 12, 23], provided that the interaction potential parameters (r_m, ε, α) are accurately calibrated. In this study, the values of interaction parameters are taken from several sources (Table 1). The interaction parameters for the main detonation products are calibrated based on experimental shock Hugoniots, which is considered the most accurate way to determine interaction parameters [24]. Considering the above, the impact of the accuracy of thermodynamic functions of state and EOS on the accuracy of prediction of detonation parameters are not analyzed in this paper.

Since the detonation parameters were calculated for the experimental densities (ρ_0) at which detonation velocities and pressures are measured, variations in density (i.e., measurement error) could have affected the experimental values of detonation velocities and pressures. On the other hand, inaccuracy in the enthalpy of formation values affects the calculation result. According to Rose [42] the enthalpies of formation can be determined experimentally with the measurement error of up to 20 kJ/mol. Rice et al. [43] found that the maximum difference between the enthalpies of formations derived by quantum mechanical calculations and those determined experimentally goes up to 148 kJ/mol, with RMS=37.7 kJ/mol. Given such a significant deviation, the question arises as to what is the influence of the variation of the enthalpy of formation on the calculated detonation parameters and what accuracy is required for reliable prediction of the detonation parameters. This is analysed below using RDX and PETN as examples. The detonation parameters are calculated for (ΔH_f^{298}+error), where ΔH_f^{298} are the enthalpies of formation of RDX and PETN given in Table 4 and the error varied from 20 to 100 kJ/mol). It should be noted that the influence of the enthalpy of formation on the calculated detonation parameters will be somewhat different for each explosive, depending on its composition and density. For both RDX and PETN an almost linear dependence of calculated D and p_{CJ} on ΔH_f^{298} is obtained (Fig. 5)

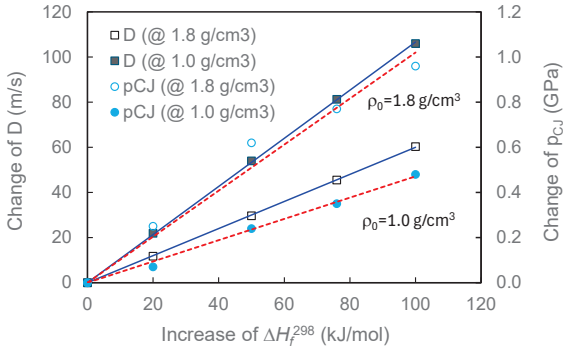

Fig. 5. Change of D and p_{CJ} at two different densities with variation of ΔH_f^{298} (note: dashed red line –p_{CJ}, solid line – D)

As follows from Fig.5, when ΔH_f^{298} increases by 100 kJ/mol, then at the density of 1.8 g/cm^3, D increases by 60 m/s (0.7%) and p_{CJ} increases by 0.96 GPa (2.8%). At the density of 1.0 g/cm^3, D increases by 106 m/s (1.8%) and p_{CJ} increases by 0.48 GPa 5.1%). In both cases, the variation of D and p_{CJ} is within measurement error (±200 m/s and ±5 GPa). Such results suggest the conclusion that ΔH_f^{298} variation has little effect on calculated D, while the effect on p_{CJ} is somewhat more significant. However, varying ΔH_f^{298} has the greatest effect on the heat of detonation (Q_d) and detonation temperature (T_d). For example, in the case of RDX, Q_d increases by about 400 kJ/kg (7%) and T_d increases by about 260 K (6.2%) when ΔH_f^{298} increases by 100 kJ/mol).

As follows from the previous discussion, different parameters affect both the experimental and calculated values of detonation velocities and pressures. When it comes to experimental results, this can result in a measurement error of several percent for detonation velocities (up to ≈200

m/s) and over 10% for pressures (up to ≈5 GPa). Such errors affect the reliability of the validation of thermochemical calculations and bring to the fore the importance of choosing accurate experimental data. Unfortunately, it is not an uncommon practice that when stating the experimental values of the detonation parameters, the authors do not provide all the necessary information (e.g., the charge size and the influence of the size on the detonation parameters, the method of initiation, measurement uncertainty, etc.).), which makes the assessment of the reliability of the results difficult. This is especially true when dealing with non-ideal explosives where the detonation parameters strongly depend on the charge size.

The results of thermochemical calculations are also affected by numerous factors, from the equation of the state of the detonation products to the charge density and enthalpy of formation. For accurate prediction of detonation parameters, it is crucial to choose an accurate equation of state, accurate enthalpies of formation of explosives, and accurate values of thermodynamic functions of the state of detonation products.

4. Conclusions

The accuracy of prediction of key detonation parameters using an analytic equation of state for EXP-6 potential fluid, incorporated in thermochemical code EXPLO5, is studied in the paper. The accuracy of prediction of detonation velocities and pressures is estimated by comparing experimental and calculated values for 48 different explosives having CHNO, CNO, HNO, and NO composition and densities in the range of 0.25-1.97 g/cm^3.

It is shown that detonation velocities for ideal explosives can be predicted with an error below 200 m/s (below 3%). The error is slightly larger in the case of NQ and TATB (which exhibit non-ideal behaviour) -predicted detonation velocities are higher by 316-463 m/s (3.9-6.0%). Statistical parameters of the correlation analysis for all 48 data points are: MAE=95.5 m/s, MAPE=1.46 %, RMSE=139.1 m/s.

The predicted detonation pressures are systematically a bit underestimated compared to the experimental (the slope of $p_{CJ\ expt.}$-$p_{CJ\ calc.}$ line equals 0.9807). Despite this, the detonation pressure can be predicted with an error of less than 2 GPa for 86% of the studied explosives, for 11.36% of the explosions the error is 2-2.5 GPa, and for only one explosive (BTF) the error is 3.75 GPa. Statistical parameters of the correlation analysis for 44 data points: MAE=0.89 GPa, MAPE= 6.29 %, RMSE=1.21 GPa.

The fact that the detonation velocity and pressure can be predicted with an error that is in most cases within the measurement error (≈200 m/s for D and ≈5 GPa for p_{CJ}), makes EXP-6 EOS suitable for application in thermochemical codes intended for detonation parameter prediction.

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