Reparametrization of the BKW Equation of State for CHNO Explosives which Release no Condensed Carbon upon Detonation

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Abstract: The BKW equation parameters and gaseous product co-volumes were reparametrized for CHNO explosives which release no condensed carbon when detonated. This estimation has led to a more reliable (correct) parameter set of the BKW equation because all of the possible errors due to the uncertainties in the phase composition and equation of state for nanoscale condensed carbon, the inhomogeneity of composite explosives, and so forth, are eliminated. The estimation was performed using an optimization database of 24 explosives, including 121 measurements of detonation velocity and pressure. Three parameters of the BKW equation and the co-volumes of 45 gaseous products were optimized. A set of 10 explosives having a small negative oxygen balance was checked. The resulting set provides a several-fold smaller error in calculating the detonation velocity and a more accurate prediction of the detonation pressure, as compared to the known sets of BKWRDX, BKWR, BKWS, and BKWC.

Keywords: thermochemical codes, explosives, detonation, BKW equation of state

1 Introduction

The Becker-Kistiakowsky-Wilson equation of state (BKW-EOS) is nowadays one of the most common equations for estimating detonation wave parameters. This equation, in its modern form, was first applied for detonation modelling by Cowan and Fickett in 1957 [1], who suggested the following form:

$$\frac{P \cdot V_g}{R \cdot T} = F(x) = 1 + x \cdot \exp(\beta \cdot x),\tag{1}$$

where: $x = \dfrac{k}{V_g \cdot (T + \theta)^{\alpha}}$ and $k = \gamma \sum_{i} x_i \cdot k_i$

Here, V_g is the molar volume of the gas phase; x_i is the molar fraction of the *i*th component (summation is made over all gaseous components of the mixture); α, β, θ, γ are empirical constants; k_i is the co-volume of the gaseous component *i*.

To find the BKW equation parameters, Cowan and Fickett [1] used data obtained from measuring the D–ρ_0 dependence on the detonation pressure at the maximum achievable density for five explosives. It was speculated that the detonation products comprised the following ingredients: H_2, CO_2, CO, H_2O, N_2, NO, and C (graphite). The equilibrium composition of the detonation products was estimated by the method of equilibrium constants. It was supposed that the condensed carbon was graphite, for which its own equation of state was proposed.

Mader [2, 3] showed that it was impossible to find a set of parameters included in the BKW equation of state that would result in a quite good reproduction of experimental values of the detonation parameters for RDX and TNT at those co-volume values that nicely reproduce experimental Hugoniot adiabats for individual detonation products. Two sets of parameters were therefore suggested: (1) for explosives having a positive or small negative oxygen balance, and (2) for explosives whose detonation products have a large amount of condensed carbon.

Finger *et al*. [4] investigated the effect of elemental composition on the detonation behaviour of explosives and made an attempt to gain a wider experimental basis for determining an improved set of coefficients included in the BKW equation. The set of parameters and co-volumes of gas molecules, referred to as BKWR, was obtained using experimental data (10 velocities, 10 pressures, and 4 temperatures of detonation) for 10 individual and composite explosives. The BKWR equation-based program accounts for 13 gaseous products (including 4 fluorine containing ones) and 1 condensed product (graphite, with an enthalpy of formation of 12 kcal/mol).

Hobbs and Baer [5, 6] optimized the BKW equation parameters with a large product species database. The estimation took into account 61 species of gaseous atoms, molecules, and radicals and was run on an optimization database covering 62 explosives at 111 initial densities. The total number of experimental measurements was 188 including 107 detonation velocities, 67 Chapman-Jouguet (C-J) pressures, and 14 temperatures. The generated set of parameters was called BKWS. In contrast to the other equations of state, the co-volumes employed in the BKWS equation relied on the molecular structures

of the gaseous components. The co-volumes were calculated using measured van der Waals radii, bond lengths, and bond angles. The three BKW equation constants β, θ, and γ were calculated in the optimization. To allow for uncertainty in measuring the C-J parameters at low density, a density weighted cost function was applied in order to optimize the BKW equation parameters.

Fried and Souers [7] used the energy of the products at different points during isentropic expansion and the total explosion energy as additional characteristics of the explosives, besides the detonation velocity and pressure at the Chapman-Jouguet point. Their optimization database was thoroughly screened and contained 32 explosives, including 27 ideal, 3 partially ideal and 2 highly non-ideal ones. The number of the relevant compounds was confined to products having at least 0.05 mol/kg concentration. The optimization parameters of the equation includes four BKW constants (α, β, γ, θ), "freezing" temperature, 3 parameters in the equation of state for condensed carbon, and 23 co-volumes of gaseous products (including 5 fluorine and 2 chlorine containing compounds). These 31 parameters were calibrated using the total error function (weighted root mean squared discrepancy) that included the following measured parameters: 32 velocities, 30 detonation pressures, and 132 energies of products during expansion. In comparison to the BKWR and BKWS equations, the resultant parameter set, called BKWC, gives a better agreement with experimental data on detonation velocity, overall detonation energy, and energy of products during adiabatic expansion.

The optimization or selection of the BKW equation parameters was also performed by other authors [8-11]. Separate parameters of the BKW equation were selected on the basis of experimental data for the detonation parameters of a few explosives, the composition of the gaseous products being confined to 9 basic compounds for CHNO explosives.

The presence of condensed carbon in the detonation products significantly complicates the calculation of detonation parameters. This is due to the fact that condensed carbon exists in the nanoscale state in the detonation products and may be present in different phase states − graphite or diamond [12]. The properties of these nanodispersed phases (heat capacity, entropy, compressibility, thermal expansion, *etc*.) in the range of detonation pressures and temperatures are currently unknown. Hence, either the massive body equation of state [1] or simple empirical relations without concretizing the phase composition [7] are used to describe the behaviour of condensed carbon.

Detonation waves with the phase composition of carbon taken into account were first calculated by Gubin *et al*. [13]. Four BKW equation parameters and the co-volumes of 9 basic gaseous products (for CHNO explosives) were optimized

on the basis of experimental data on the detonation rates of 60 explosives with due account for the formation of graphite or diamond in the detonation products. The BKWRR parameter set obtained ensures considerably higher accuracy in predicting the detonation velocity compared to BKWR.

In all of the existing calculation algorithms, the BKW-EOS parameters were optimized on optimization explosive databases that generally involve individual and composite explosives with both positive and negative oxygen balances. Fried and Souers noticed that it is difficult to ascertain which part of the discrepancy between calculation and experiment occurs due to experimental errors and which part stems from the inadequate description of experimental data by the chosen equation of state [7]. It should be noted that many more factors, which are not taken into account at all, contribute to the overall estimated error.

Those are, first of all, the phase composition and properties of condensed carbon present in the detonation products of many explosives. As already mentioned, the existing algorithms describe properties of condensed carbon in a very simplified manner, without due regard to its actual phase composition and properties. It is worth noting that for some explosives with very high detonation temperatures (*e.g.*, benzotrifuroxane), condensed carbon can exist in the liquid phase whose properties are practically unknown.

Secondly, for heterogeneous composite explosives, the decay products of molecules of the different initial ingredients have no time to intermix within the chemical reaction zone of the detonation wave [14]. The ingredients of composite explosives are decomposed in different micro-volumes, and the final composition of the detonation products is formed in the later stages during adiabatic expansion of the products. In this respect, a question arises as to whether it is appropriate to use a unified (general) brutto formula in calculating the detonation parameters of heterogeneous composite explosives or to find the detonation velocity over the tangency point of the Rayleigh line with the overall (homogeneous) Hugoniot adiabat. For homogeneous solutions, it is necessary to take account of the dissolution heat, disassociation, and the formation of associates, but these data are not always known.

In this respect, the BKW equation parameters can only be correctly determined if the said complicating factors are absent. In other words, the optimization of the BKW equation parameters on an optimization database that includes explosives whose detonation products do not contain condensed carbon will result in distortion and errors in estimating the BKW-EOS parameters and the co-volumes of gaseous molecules when an improper equation of state for condensed carbon is used.

To this end, reparametrization of the BKW equation has been performed for

an optimization database that comprises only individual CHNO explosives (and also explosives lacking one or several elements) which do not release condensed carbon upon detonation.

2   Calculation Procedure

For the correct determination of parameters, the database size must be vast enough to reduce the effect of errors in separate measurements. In this respect, the literature data on the detonation parameters of the said explosives have been analyzed and a comparative analysis of various literary sources has been performed to reject rough deviations. The list of explosives used for the optimization of the BKW equation parameters and some of their properties are given in Table 1. A total of 24 explosives are included in the optimization database.

The optimization database encompasses explosives whose detonation products are *a priori* known to contain no condensed carbon. These are explosives bearing no carbon in the initial molecule and those having a positive oxygen balance (OB). To these substances were added explosives with zero and small negative oxygen balances, whose explosion products have no condensed carbon, as reported in various literature sources. Among these, most notable, is PETN, for which there are numerous reliable experimental data on both detonation velocity and other parameters. When it is exploded at an initial density of 1.69-1.72 g/cm^3, condensed carbon was not detected in the explosion products [24]. It should be noted that the amount of condensed carbon in the detonation products diminishes with decreasing density of an explosive, and condensed carbon disappears from the detonation products for an explosive with a small oxygen balance at a density below a certain value. An example of such an explosive is HMX, whose detonation products do not contain condensed carbon in spite of the negative oxygen balance at densities of 1.2 g/cm^3 and lower [24]. Meanwhile, when HMX with a density of 1.89 g/cm^3 is exploded, the amount of solid carbon in the detonation products is about 3.3 moles per 1 kg explosive [24]. This is also the case for RDX, an analogue of HMX, which liberates solid carbon at densities above 1.15 g/cm^3 [25]. When a CL-20 charge having a density of 1.965 g/cm^3 was detonated in a gold annulus, condensed carbon was not detected in the detonation products, as reported in [26].

Table 1.   List of explosives used

Explosive		Formula	OB [%]	$\Delta_f H°_{298.15}$ [kJ/mol]
NO	Nitrogen oxide	NO	+53.32	77.46 [15]
HN3	Hydrazoic acid	HN_3	−18.59	269.32 [16]
HA	Hydrazinium azide	$N_2H_4 \cdot HN_3$	−53.28	246.44 [17]
AN	Ammonium nitrate	$H_4N_2O_3$	+19.99	−365.56 [18]
TNM	Tetranitromethane	CN_4O_8	+48.97	36.82 [19]
MN	Methylnitrate	CH_3NO_3	−10.38	−154.39 [19]
NU	Nitrourea	$CH_3N_3O_3$	−7.61	−281.16 [19]
DNQ	1,2-Dinitroguanidine	$CH_3N_5O_4$	+5.37	0.00 [20]
MEDINA	Methylene dinitramine	$CH_4N_4O_4$	0.00	−62.07 [21]
HNE	Hexanitroethane	$C_2N_6O_{12}$	+42.66	119.66 [22]
EGDN	Ethyleneglycol dinitrate	$C_2H_4N_2O_6$	0.00	−242.75 [18]
NG	Nitroglycerin	$C_3H_5N_3O_9$	+3.52	−372.38 [19]
RDX	Cyclotrimethylene trinitramine	$C_3H_6N_6O_6$	−21.61	70.29 [19]
DNDF	Dinitrodifuroxanyl	$C_4N_6O_8$	0.00	423.00 [23]
DNDAF	Dinitrodiazenofuroxan	$C_4N_8O_8$	0.00	670.28 [23]
Sorguyl	1,3,4,6-Tetranitroglycouril	$C_4H_2N_8O_{10}$	+4.97	41.84 [19]
BTNEN	Bis(trinitroethyl)nitramine	$C_4H_4N_8O_{14}$	+16.49	−27.63 [18]
HMX	Cyclotetramethylene tetranitramine	$C_4H_8N_8O_8$	−21.61	75.02 [18]
BTNEU	Bis(trinitroethyl)urea	$C_5H_6N_8O_{13}$	0.00	−321.74 [18]
PETN	Pentaerythritol tetranitrate	$C_5H_8N_4O_{12}$	−10.12	−532.20 [19]
HNB	Hexanitrobenzene	$C_6N_6O_{12}$	0.00	200.00 [23]
TNETB	2',2',2'-Trinitroethyl 4,4,4-trinitrobutyrate	$C_6H_6N_6O_{14}$	−4.14	−497.90 [6]
CL-20	Hexanitrohexaazaisowurtzitane	$C_6H_6N_{12}O_{12}$	−10.95	403.36 [18]
MXN	Mannitol hexanitrate	$C_6H_8N_6O_{18}$	+7.08	−636.10 [18]

These examples, of course, do not prove that condensed carbon is absent at the Chapman-Jouguet (C-J) point for the examined explosives with a small negative oxygen balance; however, its amount must be low and must not significantly affect the detonation velocity and pressure. Nevertheless, the amount of condensed carbon was controlled at each step of the optimization, and when it appeared at any point for any explosive, that point was excluded from the optimization database.

Of the various experimental parameters characterizing detonation, the C-J detonation velocity and pressure were used. Table 2 sets out the number of

experimental points for each explosive from the optimization database and the density range taken to perform optimization.

Table 2.   Density range and number of experimental points for the explosives used

Explosive	Density range [g/cm³]	Number of experimental points		Ref.
		D	P	
NO	1.28; 1.294	2	1	[27, 28]
HN3	1.127	1	1	[29]
HA	0.68	1	-	[30]
AN	0.83; 1.00	2	-	[31, 32]
TNM	1.64	1	1	[6]
MN	1.208	1	-	[33]
NU	1.10	1	-	[34]
DNQ	1.81-1.87	2	2	[20]
MEDINA	1.68	1	-	[35]
HNE	1.86	1	-	[22]
EGDN	1.50	1	-	[33]
NG	1.60	1	1	[6]
RDX	0.70-1.15	10	6	[6, 25]
DNDF	1.96	1	-	[22]
DNDAF	1.77-1.94	3	-	[22]
Sorguyl	1.95	1	-	[18]
BTNEN	0.92-1.96	10	-	[36-39]
HMX	0.75-1.00	2	2	[6, 25]
BTNEU	1.00-1.86	4	-	[34, 40]
PETN	0.60-1.77	25	18	[41-43]
HNB	1.965-2.00	3	1	[44-46]
TNETB	1.23-1.76	10	-	[47, 48]
CL-20	1.94; 1.96	2	-	[49, 50]
MXN	1.73-1.75	2	-	[18]
Total:		88	33	

As the optimization database comprises a lot of diverse explosives, including "exotic" ones (NO, HN3, HA), one should expect considerable variations of temperature and pressure upon detonation. To adequately describe these diverse conditions, it was necessary to take into consideration as many gaseous products as possible. In the present work, the optimization was performed using 49

gaseous products, including atoms, molecules, and radicals. Ionization of the products was ignored. Thermodynamic data for gases under standard conditions were taken from the handbook [51], whereas other data [52] were used in case a compound was missing from the handbook.

As the optimization criterion, an error function representing the weighted root mean squared discrepancy was taken:

$$R = \sqrt{\frac{1}{(N+L)}\left[\sum_{i=1}^{N} w_D^2 \left(\frac{D_i^c - D_i^m}{D_i^m}\right)^2 + w_P^2 \sum_{i=1}^{L}\left(\frac{P_i^c - P_i^m}{P_i^m}\right)^2\right]} \quad (2)$$

where N, L are the number of experimental points for the detonation velocity (D) and pressure (P); w_D, w_P are the weight coefficients of the detonation parameters. Superscripts c and m are the calculated and measured detonation properties, respectively. The following weight coefficients were taken: $w_D = 0.9$ and $w_P = 0.1$. This ratio is determined by the fact that the error in an experimental measurement of the detonation pressure exceeds that in the measurement of the detonation rate by about an order of magnitude [7].

The function was minimized by the Nelder-Mead simplex method for multidimensional minimization [53]. The function described by this equation relies on 24 explosives at 88 initial densities and 121 measurements that included 88 velocities and 33 pressures.

3   Results and Discussion

Since condensed carbon is absent in the detonation products for all of the compounds used in the optimization, the concentration of atomic gaseous carbon is extremely low and appreciably lower than the equilibrium pressure of carbon vapour over the condensed phase. At the same time, the oxygen content in the original explosives and, correspondingly, in their detonation products is sufficiently high. Therefore, the concentration of unoxidized compounds (such as C_2−C_5, C_2H_4, C_2H_6, N_2H_2, N_2H_4) in the detonation products is very low. The amount of such compounds must be substantially greater for explosives whose detonation products contain condensed carbon (like TNT). The detonation products also have a low content of compounds that are themselves strong oxidizers (N_2O_4, HNO_3). Without incurring a significant error, these compounds can be omitted during the calculations for explosives whose detonation products contain no condensed carbon, and their more precise measurement can and must

be made for explosives that release condensed carbon when detonated. The co-volumes of the gaseous products obtained as a result of the optimization are summarized in Table 3. The amounts of these gases in the detonation products for all of the optimization points is greater than 10^{-4} moles. For the optimization set of explosives used, the number of these gases was 34. Parameter γ in BKW Equation (1) enters into all of the co-volumes as a constant in a product form. As the co-volumes of all of the gaseous compounds change during the calculation, the optimization of parameter γ is pointless. The parameter γ was therefore taken as a simple conversion coefficient that makes dimensions in the BKW equation consistent: 10.0 $cm^3 \cdot K^\alpha$. Thus, the co-volumes of all of the gaseous products obtained exceed those of other authors by a value reported elsewhere. During the calculations, the BKW equation parameters α, β, θ and the co-volumes of 45 gaseous compounds (the co-volumes of 11 substances whose amount is not greater than 10^{-4} moles are not shown in Table 3) were optimized.

The following equation parameters were derived: $\alpha = 0.500856$, $\beta = 0.504859$, $\gamma = 10.0$ $cm^3 \cdot K^\alpha$, and $\theta = 5032.87$ K.

**Table 3.** Co-volume factors of gaseous products whose amount is not greater than 10^{-4} moles

Species	Co-volume	Species	Co-volume	Species	Co-volume
H	5	CO_2	502	N	81
HO	89	CHO	410	NO	394
HO_2	455	CH_2O	384	N_2	341
H_2	11	CH_2O_2	522	NO_2	594
H_2O	226	CH_4O	804	N_2O	802
H_2O_2	714	CN	254	NH_2	476
C	83	HCN	387	NH_3	697
CH_2	113	CNO	399	HNO	651
CH_3	275	HNCO	836	HNO_2	720
CH_4	190	O	119	NH_2OH	336
C_2H_2	193	O_2	305		
CO	359	O_3	377		

The calculated detonation rates plotted against the experimental ones for the chosen optimization explosive database is shown in Figure 1. It is seen that these values are in good agreement for all of the explosives, including the "exotic" ones.
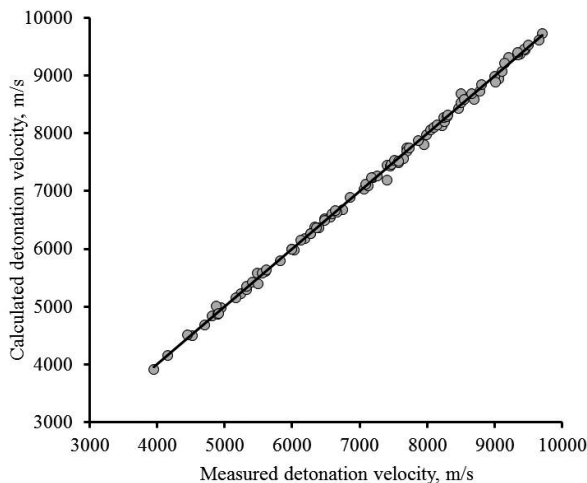
Figure 1.   Calculated detonation velocity versus the experimental value.

Deviations of the calculated detonation velocities and pressures at the Chapman-Jouguet point from the experimental values, as a function of density, are shown in Figures 2 and 3 respectively. Most of the calculated detonation velocities fall within the range of ± 1% relative to the measured values (85.2% of all of the calculated points), and only 3 values (3.4%) have a discrepancy exceeding 2%. The detonation pressure has a significantly higher deviation because the measurement error for this parameter is greater by an order of magnitude. 85% of all of the calculated points lie in the range of ± 10% (pressure measurement error [7]).
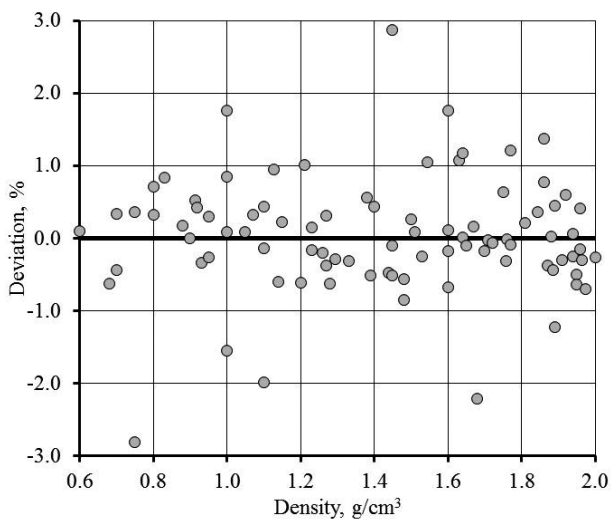
Figure 3. Deviation of the calculated C-J detonation pressure from the experimental data as a function of the explosive density.
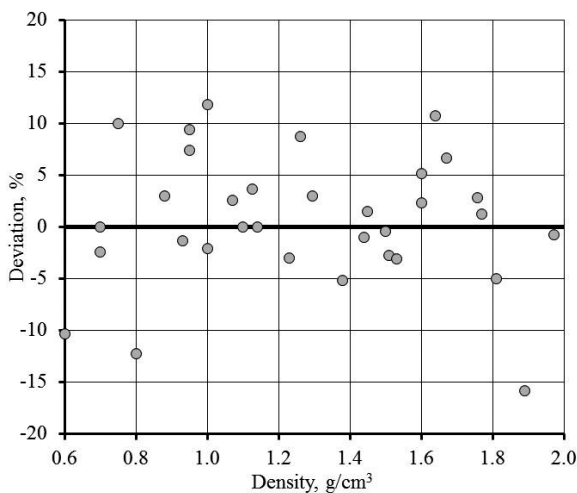
Figure 3. Deviation of the calculated C-J detonation pressure from the experimental data as a function of the explosive density.

The resultant set of the BKW equation parameters and the co-volumes of the gaseous molecules enables considerably higher accuracy to be obtained in calculating the detonation velocity and pressure for explosives releasing no condensed carbon when compared to the other sets. Table 4 compares the

errors in calculating these parameters for the set obtained (BKWNV) with BKWRDX [3], BKWR [4], BKWS [5], BKWC [7]. It should be noted that the last set was derived from the optimization of experimental data by using many gaseous products in a manner similar to the present work. Calculations with the BKWTNT set [3] were not made because this equation is intended for estimating the detonation parameters of explosives whose detonation products are rich in condensed carbon.

Table 4. Comparison of the calculated and experimental detonation rates and pressures for 24 individual explosives (symbols Δ and δ stand for the average absolute and average relative deviations of the calculated from the experimental value, respectively)

EOS	Detonation rate		Detonation pressure	
	ΔD, [m/s]	δD, [%]	ΔP, [kbar]	δP, [%]
BKWNV	39.5	0.57	7.7	4.77
BKW-RDX [3]	255.4	3.86	9.8	9.6
BKWR [4]	330.7	5.24	16.2	14.0
BKWS [5]	306.4	4.60	10.6	10.0
BKWC [7]	133.6	1.84	9.6	6.0

The comparison of the calculation results obtained using the common sets demonstrates that the BKWC equation, compared with the other known sets, provides the highest accuracy in predicting the detonation velocity and pressure for explosives containing no condensed carbon in the detonation products. The BKWNV set derived in the present study provides an approximately 3-fold smaller error in calculating the detonation rate and higher accuracy in predicting the detonation pressure, as compared to the BKWC equation.

In a comparative evaluation of the calculation errors listed in Table 4, it is important to bear in mind that the BKWNV equation represents a specific set derived using a comparatively small optimization database in which the explosives are limited to those having no condensed carbon at the Chapman-Jouguet point. The question arises as to whether it is possible to apply the given set to substances not included in the examined database. The selection of explosives for such a verification represents a challenging task, because almost all of the explosives whose detonation products contain no condensed carbon are listed in Table 1. The selection of test explosives from the available data was therefore carried out taking into account a minimal content of condensed carbon in the detonation products. In doing so, mistakes that are associated with the use of the equation of state for condensed carbon and describe its properties

inaccurately are reduced to a minimum. In this connection, the selection was carried out from among explosives with a relatively small negative oxygen balance, which was less than half that of TNT (OB = −73.96%). Moreover, with other conditions being equal, preference was given to experimental data at a low density of the explosive charge. The properties of the explosives chosen for verification are summarized in Table 5.

Table 5. List and properties of explosives used to check the BKWNV equation

Explosive		Formula	OB [%]	$\Delta_f H°_{298,15}$ [kJ/mol]
NQ	Nitroguanidine	$CH_4N_4O_2$	−30.75	−92.88 [19]
NTO	3-Nitro-1,2,4-triazole-5-one	$C_2H_2N_4O_3$	−24.60	−100.75 [18]
FOX-7	1,1-Diamino-2,2-dinitroethylene	$C_2H_4N_4O_4$	−21.61	−133.90 [18]
EDNA	Ethylenedinitramine	$C_2H_6N_4O_4$	−31.98	−103.34 [19]
FOX-12	N-Guanylurea-dinitramide	$C_2H_7N_7O_5$	−19.13	−356.00 [18]
EDDN	Ethylenediamine dinitrate	$C_2H_{10}N_4O_6$	−25.79	−651.87 [19]
TNAZ	1,3,3-Trinitroazetidine	$C_3H_4N_4O_6$	−16.66	+36.40 [19]
DINGU	1,4-Dinitroglycouril	$C_4H_4N_6O_6$	−27.57	−312.96 [19]
DINA	Dihydroxyethylnitramine dinitrate	$C_4H_8N_4O_8$	−26.65	−275.72 [19]
HCO	1,3,3,5,7,7-Hexanitro-1,5-diazacyclooctane	$C_6H_8N_8O_{12}$	−16.66	−27.34 [54]

Since there are no experimental data on detonation pressure, the calculation errors for different sets were evaluated on the basis of detonation velocity alone. The results of such a comparison are collected in Table 6. For the BKWNV equation when condensed carbon (graphite) is present in the detonation products, the condensed carbon properties were described by the equation suggested by Cowan and Fickett [1], with an enthalpy of formation of 50.2 kJ/mol.

Table 6. Experimental and calculated detonation rates

Explosive	Experiment	BKW-RDX	BKWR	BKWS	BKWC	BKWNV
NQ ρ_0=1.0	5460 [55]	5801 (+6.2)	5938 (+8.7)	5521 (+1.1)	5415 (−0.8)	5392 (−1.2)
NTO ρ_0=1.0	5269 [56]	5468 (+3.8)	5644 (+7.1)	5266 (+0.1)	5300 (+0.6)	5260 (−0.2)

Explosive	Experiment	BKW-RDX	BKWR	BKWS	BKWC	BKWNV
FOX-7 ρ_0=1.78	8405 [57]	8657 (+3.0)	8683 (+3.3)	8558 (+1.8)	8422 (+0.2)	8386 (−0.2)
EDNA ρ_0=0.98	5760 [58]	6131 (+6.4)	6368 (+10.5)	6029 (+4.7)	5791 (+0.5)	5783 (+0.4)
FOX-12 ρ_0=1.666	7970 [59]	8249 (+3.5)	8176 (+2.6)	8009 (+0.5)	7821 (−1.9)	8012 (+0.5)
EDDN ρ_0=1.30	6660 [34]	6805 (+2.2)	7030 (+5.6)	7090 (+6.5)	6244 (−6.2)	6654 (−0.1)
TNAZ ρ_0=1.83	8730 [60]	8713 (−0.2)	9056 (+3.7)	8977 (+2.8)	9010 (+3.2)	8736 (+0.1)
DINGU ρ_0=0.8	4500 [32]	4829 (+7.3)	4997 (+11.0)	4728 (+5.1)	4588 (+2.0)	4486 (−0.3)
DINA ρ_0=1.0	5950 [55]	6132 (+3.1)	6412 (+7.8)	6163 (+3.6)	5925 (−0.4)	5866 (−1.4)
HCO ρ_0=1.792	8520 [54]	8524 (+0.1)	8849 (+3.9)	8741 (+2.6)	8749 (+2.7)	8549 (+0.3)
δD, [%]	−	3.6	6.4	2.9	1.9	0.5

The results outlined in Table 6 show that the BKWC equation is the best from among the known sets in terms of estimating the detonation rates for explosives having a small negative oxygen balance. However, in this case, as with the explosives collected in Table 1, the BKWNV equation ensures an approximately 4-fold higher accuracy in calculating the detonation rate as compared to the BKWC equation, besides the other equations. The errors obtained are at the level of errors in the most accurate experimental data.

Mention should be made of the limits in applicability of the BKWNV equation. This equation can be used for explosives having an oxygen balance (OB) over −32% (carbon being present in the composition) or for carbon-free explosives; in this case, the equation of state for graphite can be employed [1]. The determination of the best set of coefficients of the BKW equation for any explosive, including those whose detonation products have condensed carbon, is a more complicated problem that must be resolved in several steps. Firstly, it is necessary to define a realistic form of the equation of state for nanodispersed graphite (soot) and optimize the coefficients of this equation for explosives at low and moderate densities. This limitation is attributed to the possible formation of the nanodiamond phase of carbon when powerful explosives are detonated at high densities of the explosive charge [61]. The equation of state for graphite [1] does not describes its properties quite correctly when pressures and temperatures

are high: it exaggerates compressibility and affords unrealistic dependences of the thermal expansion coefficient and bulk modulus on pressure and temperature.

The second step is to choose an equation of state for nanodiamond and optimize its coefficients. In doing so, the calculation must take into account the fact that the two nanodispersed phases, diamond and graphite (soot), might be present simultaneously in the detonation products, because it does not seem possible to select explosives whose detonation products are *a priori* known to only contain nanodiamond.

In the third step, similar procedures have to be performed considering the formation possibility of liquid carbon for explosives with very high detonation temperatures (benzotrifuroxane, trinitrotriazidobenzene). These findings will afford the opportunity to not only significantly enhance the accuracy in calculating the detonation parameters, but also model the phase composition of condensed carbon and thereby optimize the detonation synthesis of nanodiamonds.

4   Conclusions

The present work was aimed at estimating the parameters of the BKW equation and the co-volumes of the gaseous products for individual explosives whose detonation products do not contain condensed carbon (at the C-J point). In particular this calculation has led to the most reliable (correct) parameter set of the BKW equation because, in this case, possible errors associated with uncertainties in the phase composition and the equation of state for condensed nanocarbon, the inhomogeneity of composite explosives, and so on, are eliminated.

The parameters have been determined for an optimization database involving almost all of the reliable data available in the literature for such explosives. The resulting parameter set provides an estimated error for the detonation parameters at the level of the most accurate experimental data. It can be deduced that, as applied to at least the explosives used, the BKW equation describes the gas phase properties under detonation conditions quite adequately.

To extend this deduction to all classes of explosives, including those having a discernibly negative oxygen balance, it is necessary to discover the properties of, and a realistic form of the equation of state for, the different condensed carbon phases that are generated upon detonation. Afterwards, refinement of the co-volumes of the gaseous products formed in trace amounts can be carried out.

Addressing these problems will improve the calculation accuracy and allow one to assess the adequacy of using the BKW equation in respect to detonation waves.

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