The Role of Product Composition in Determining Detonation Velocity and Detonation Pressure

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Abstract: Four sets of rules for predicting the detonation product compositions of explosives have been investigated: the Kamlet-Jacobs, the Kistiakowsky-Wilson, the modified Kistiakowsky-Wilson and the Springall-Roberts. These can result, for a given compound, in significantly differing detonation products and amounts of heat release. However the resulting detonation velocities D and detonation pressures P obtained for the compound using the Kamlet-Jacobs equations are generally quite similar, with the Kamlet-Jacobs rules leading to the D and P that are, on average, closest to the experimental. The fact that the variations among the D and P values are relatively small can be attributed to a balancing of opposing effects relating to the quantities of gaseous products and the heat releases. Accordingly, obtaining reasonable accuracy for D and P does not necessarily imply corresponding accuracy for the product composition and heat release that were used. The analysis presented explains the observations that D and P can be correlated with loading density alone, even though product compositions are known to change with density.

Keywords: detonation velocity, detonation pressure, density, detonation product composition, detonation heat release

1   Detonation Performance

Two key criteria for evaluating explosives are detonation velocity (D) – the stable velocity of the shock front that characterizes detonation – and detonation pressure (P) – the stable pressure that is developed behind the front [1-6]. It is desirable that both D and P have high values, although this must be reconciled with the somewhat contradictory goal of low sensitivity (*i.e.* low vulnerability

to unintended detonation caused by an accidental stimulus, such as impact, shock, friction, *etc.*) [7]. Difficulty of synthesis and processability are other very important considerations.

What determines detonation velocity and detonation pressure? Some understanding of this is clearly needed if new explosive formulations with improved detonation performance are to be developed. In this respect, a very significant contribution was made by Kamlet and Jacobs [8]. They identified four factors that explicitly affect D and P:

(1) the number of moles N of gaseous detonation products per gram of explosive,
(2) their average molecular mass M_{ave} in g/mol,
(3) the magnitude of the heat release Q for the detonation reaction, in calories per gram of explosive, and
(4) its loading density ρ in g/cm^3.

Kamlet and Jacobs expressed D and P in terms of these four quantities by the empirical relationships:

$$D \text{ (mm/}\mu\text{s)} = 1.01[N^{0.5}M_{ave}^{0.25}Q^{0.25}(1 + 1.30\rho)] \tag{1}$$
$$P \text{ (kbar)} = 15.58[NM_{ave}^{0.5}Q^{0.5}\rho^2] \tag{2}$$

Eqs. (1) and (2), which are designed specifically for C,H,N,O-containing explosives, have been shown to have good accuracy and reliability in comparisons with experimental D and P [8-13].

If one mole of an explosive compound has mass M and produces n moles of gaseous products upon detonation, then N = n/M. If all of the compound has been converted to gaseous products, then M_{ave} = M/n, so that N and M_{ave} are reciprocals of each other, N = 1/M_{ave}. However the detonation of C,H,N,O explosives often yields some solid carbon, in which case M_{ave} = (M - c)/n, where c represents the mass of carbon produced per mole of explosive. Then N and M_{ave} are not exact reciprocals, but have only a roughly inverse relationship for a given M. Note that they appear to different powers in Eqs. (1) and (2).

The quantity that is raised to the highest powers in these equations is the loading density ρ, and it is indeed generally viewed as an important determinant of D and P. However it is not as dominant, on a relative basis, as Eqs. (1) and (2) may suggest. A good example is provided by the explosives RDX (**1**, 1,3,5-trinitro-1,3,5-triazacyclohexane) and TATB (**2**, 2,4,6-triamino-1,3,5-trinitrobenzene). At a loading density of 1.80 g/cm^3, RDX has D = 8.754 mm/μs and P = 347 kbar [14] while TATB at a much higher density of 1.895 g/cm^3 has lower D and P, 7.86 mm/μs and 315 kbar, respectively. The primary reason is that RDX has a much higher Q than does TATB, as will be seen in Table 3. The magnitude of

ρ tends to vary considerably less than that of Q from one C,H,N,O explosive to another [3, 8, 13], and accordingly the density does not differentiate between compounds as well as might be inferred from Eqs. (1) and (2).

1   **2**   **3**
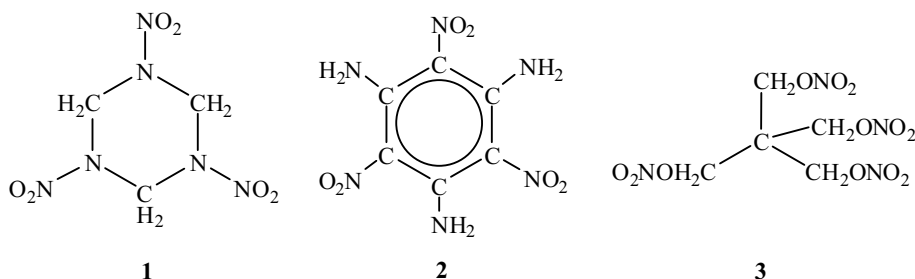
To predict D and P via Eqs. (1) and (2), it is necessary to assign values (on some basis) to N, M_{ave}, Q and ρ. If the detonation products are known or assumed, then N and M_{ave} follow immediately. Since Q = -ΔH for the detonation reaction, it can be obtained from the respective enthalpies of formation. Those of the possible products are usually accurately known [15, 16], and computational methods are available for obtaining $\Delta H_f°$(solid) of the explosive [17, 18] and also its crystal density [19-21], if these have not been determined. (In practice, the loading density may be less than that of the pure crystal, but if the former is not known then the latter is used in calculating D and P.)

A key issue that remains to be addressed is the composition of the detonation products. Detonation processes can be quite complex and may involve a variety of intermediates [22], as well as equilibria such as $2CO(g) \leftrightarrow CO_2(g) + C(s)$ and $H_2(g) + CO(g) \leftrightarrow H_2O(g) + C(s)$ [8]. Computer codes, involving equations of state, have been designed to predict the products and to calculate D and P [14, 23-25]. Analyses with these codes have shown, however, that the situation is usually less complicated than might have been anticipated. For most C,H,N,O secondary explosives, the final detonation products are likely to be almost entirely some combination of $N_2(g)$, $H_2O(g)$, $CO(g)$, $CO_2(g)$, $H_2(g)$ and C(s) [8, 13, 14, 26]. At low loading densities, the proportions of CO and H_2 increase and there may also appear some – usually very small – amounts of gases such as O_2, NH_3, NO and CH_4. (Others, *e.g.* formic acid, may also form under some conditions of temperature and pressure [27].) For instance, the detonation products of one mole of PETN (**3**, pentaerythritol tetranitrate) at ρ = 1.77 g/cm³ are given by the BKW code [14] as (in moles) 2.00 $N_2(g)$, 4.00 $H_2O(g)$, 3.89 $CO_2(g)$, 0.223 CO(g) and 0.89 C(s). At ρ = 0.50 g/cm³, they are 1.93 $N_2(g)$, 3.73 $H_2O(g)$, 2.81 $CO_2(g)$, 2.188 CO(g), 0.167 $H_2(g)$, 0.072 $O_2(g)$, 0.001 $NH_3(g)$, 0.134 NO(g) and

0.0 C(s). Thus the main effect of considerably lowering the loading density is a marked loss of CO_2 and gain of CO.

This and other examples [8, 13, 14, 26] show that the detonation products of C,H,N,O explosives can usually be approximated quite well as varying proportions of $N_2(g)$, $H_2O(g)$, $CO_2(g)$, $CO(g)$, $H_2(g)$ and C(s). If there were some means of satisfactorily predicting these proportions in any given case, then it could be used in conjunction with Eqs. (1) and (2) to calculate D and P relatively quickly and easily, while also achieving some direct insight into factors that govern these quantities. Our objective in this study has been to examine several proposed procedures for forecasting the compositions of detonation products.

2 Rules for Predicting Detonation Products of C,H,N,O Explosives

A useful property of an explosive, in the context of detonation product composition, is its "oxygen balance" (OB) [3, 6, 28-30]. This is a measure of the extent to which the oxygens in the molecule are sufficient to completely oxidize all of the hydrogens to H_2O and the carbons to CO_2. If the number needed for this is x and the number actually available is y, then y-x gives the excess or deficiency of oxygens with respect to complete oxidation. This is expressed as a mass percent:

$$OB = \frac{(y-x)(\text{atomic mass of oxygen})(100)}{\text{total molecular mass}} \qquad (3)$$

Thus OB = 0% means that there is exactly enough oxygen for complete oxidation to H_2O and CO_2; OB > 0% indicates an excess and OB < 0% a deficiency.

If a C,H,N,O explosive has OB = 0%, then its primary detonation products for $\rho > 1.6$ g/cm^3 can be taken to be $N_2(g)$, $H_2O(g)$ and $CO_2(g)$. However most C,H,N,O secondary explosives have OB < 0%, and accordingly do not contain enough oxygens for complete oxidation of the hydrogens and carbons. Then the products may include, in addition to $N_2(g)$ and $H_2O(g)$, some combination of $CO_2(g)$, $CO(g)$, $H_2(g)$ and C(s).

Several different sets of rules have been proposed for predicting the detonation products of C,H,N,O explosives with OB < 0% and loading densities near the pure crystal values. All of them agree that whatever nitrogens are present will form $N_2(g)$. To arrive at the amounts of the other products, each set of rules

gives a series of steps to be followed sequentially.

1) Kamlet-Jacobs (KJ) [8]: (a) Convert hydrogens to $H_2O(g)$. (b) Use remaining oxygens to form $CO_2(g)$. No CO(g) is anticipated.
2) Kistiakowsky-Wilson (KW) [3, 31]: (a) Convert carbons to CO(g). (b) Use remaining oxygens to form $H_2O(g)$. (c) If any oxygens still remain, oxidize CO(g) to $CO_2(g)$.
3) Modified Kistiakowsky-Wilson (mod-KW) [3, 31]: (a) Convert hydrogens to $H_2O(g)$. (b) Use remaining oxygens to form CO(g). (c) If any oxygens still remain, then oxidize CO(g) to $CO_2(g)$.
4) Springall-Roberts (SR) [3, 31]: First three steps are same as Kistiakowsky-Wilson. (d) Convert one-third of the CO(g) that is present after (c) to $CO_2(g)$ and C(s). (e) Convert one-sixth of the CO(g) that is present after (c) to $H_2O(g)$ and C(s).

Each of the steps prescribed by any one of the sets of rules can of course be carried out only to the extent that the respective atoms are available. Whatever carbons remain unused will be present as the solid.

By the Kamlet-Jacobs rules, all carbons will go either to $CO_2(g)$ or C(s). In contrast, the other three procedures provide for the possibility of CO(g) as well. The KW and the mod-KW differ in whether the oxygens should be converted first to CO(g) or to $H_2O(g)$. According to Akhavan [3], the mod-KW rules should be used instead of the KW when the oxygen balance is more negative than -40%, *i.e.* when the compound is very deficient in oxygens.

We have applied these four sets of rules to obtain the predicted detonation products for each of a group of 14 C,H,N,O explosives. The compounds are listed in Table 1, along with their molecular masses, experimental solid phase enthalpies of formation, a set of loading densities and the respective oxygen balances. All 14 compounds have OB < 0%. The most oxygen-balanced (*i.e.* OB closest to 0%) are CL-20 and PETN, the least are HNS and TNT.

In Table 2 are the detonation products of each explosive as obtained by each set of rules. They all predict the same amount of N_2 in each case, and for the first five compounds, they agree on the H_2O. These five compounds have OB less negative than -40% (Table 1), and the KW and mod-KW procedures predict exactly the same products. However NQ also has OB less negative than -40%, but the KW and mod-KW differ for this as well as for all of the compounds with OB more negative than -40%.

Table 1. Experimental and stoichiometric properties of compounds

Compound[a]	M, g/mol	ρ,[b] g/cm^3	$\Delta H_f^\circ(s)$[c] kcal/mol	OB, %[d]
ε-CL-20, $C_6H_6N_{12}O_{12}$	438.19	2.04[e]	90.2	-11.0
HMX, $C_4H_8N_8O_8$	296.16	1.90	24.5	-21.6
FOX-7, $C_2H_4N_4O_4$	148.08	1.89[f]	-32.0	-21.6
RDX, **1**, $C_3H_6N_6O_6$	222.12	1.80	18.9	-21.6
PETN, **3**, $C_5H_8N_4O_{12}$	316.14	1.77	-128.7	-10.1
NQ, $CH_4N_4O_2$	104.07	1.629	-20.7	-30.7
TATB, **2**, $C_6H_6N_6O_6$	258.15	1.895	-17.85	-55.8
Tetryl, $C_7H_5N_5O_8$	287.14	1.61[g]	9.8	-47.4
DATB, $C_6H_5N_5O_6$	243.14	1.788	-23.4	-55.9
Picric acid, $C_6H_3N_3O_7$	229.10	1.7[f]	-52.07	-45.4
Picramide, $C_6H_4N_4O_6$	228.12	1.72[f]	-17.4	-56.1
TNB, $C_6H_3N_3O_6$	213.11	1.64[g]	-8.9	-56.3
HNS, $C_{14}H_6N_6O_{12}$	450.23	1.74	16.2	-67.5
TNT, $C_7H_5N_3O_6$	227.13	1.64	-15.1	-74.0

[a]Compound names: CL-20, hexanitrohexaazaisowurtzitane; HMX, 1,3,5,7-tetranitro-1,3,5,-7-tetraazacyclooctane; FOX-7, 1,1-diamino-2,2-dinitroethylene; NQ, nitroguanidine; Tetryl, 2,4,6-trinitrophenylmethylnitramine; DATB, 2,4-diamino-1,3,5-trinitrobenzene; picric acid, 2,4,6-trinitrophenol; picramide, 2,4,6-trinitroaniline; TNB, 1,3,5-trinitrobenzene; HNS, hexanitrostilbene; TNT, 2,4,6-trinitrotoluene.
[b]Experimental densities are from Ref. 14 unless otherwise indicated.
[c]Experimental solid state enthalpies of formation are from Ref. 32.
[d]Oxygen balance is for complete conversion of oxygens to CO_2 and H_2O.
[e]Ref. 33.
[f]Ref. 30.
[g]Ref. 1.

Table 2 shows that, for the most part, the four sets of rules yield significantly different detonation product compositions for the 14 explosives. The KJ never predict CO or H_2, while the KW and mod-KW usually do not predict any CO_2. The KW produces H_2 for NQ and for all compounds having OB more negative than -40%; the mod-KW does not do so in any instance. The KW are the only rules that sometimes do not yield H_2O. In Table 2, the SR rules always give both CO_2 and CO, and often also H_2.

Table 2 includes, for each compound, the total numbers of moles of gaseous products, n, according to the different sets of rules. This is always smallest for the KJ, largest for the KW. The range of predicted n values for any given compound can be relatively large; note TATB, Tetryl, picric acid, HNS, *etc*.

Table 2. Detonation products per mole of compound as predicted by different sets of rules

Compound	Rules	Moles of detonation products						Total moles of gaseous products, n
		$N_2(g)$	$H_2O(g)$	$CO_2(g)$	$CO(g)$	$H_2(g)$	$C(s)$	
CL-20	KJ	6.00	3.00	4.50	---	---	1.50	13.50
	KW	6.00	3.00	3.00	3.00	---	---	15.00
	mod-KW	6.00	3.00	3.00	3.00	---	---	15.00
	SR	6.00	3.00	3.50	2.00	---	0.50	14.50
HMX	KJ	4.00	4.00	2.00	---	---	2.00	10.00
	KW	4.00	4.00	---	4.00	---	---	12.00
	mod-KW	4.00	4.00	---	4.00	---	---	12.00
	SR	4.00	4.00	0.67	2.67	---	0.67	11.33
FOX-7	KJ	2.00	2.00	1.00	---	---	1.00	5.00
	KW	2.00	2.00	---	2.00	---	---	6.00
	mod-KW	2.00	2.00	---	2.00	---	---	6.00
	SR	2.00	2.00	0.33	1.33	---	0.33	5.67
RDX	KJ	3.00	3.00	1.50	---	---	1.50	7.50
	KW	3.00	3.00	---	3.00	---	---	9.00
	mod-KW	3.00	3.00	---	3.00	---	---	9.00
	SR	3.00	3.00	0.50	2.00	---	0.50	8.50
PETN	KJ	2.00	4.00	4.00	---	---	1.00	10.00
	KW	2.00	4.00	3.00	2.00	---	---	11.00
	mod-KW	2.00	4.00	3.00	2.00	---	---	11.00
	SR	2.00	4.00	3.33	1.33	---	0.33	10.67
NQ	KJ	2.00	2.00	---	---	---	1.00	4.00
	KW	2.00	1.00	---	1.00	1.00	---	5.00
	mod-KW	2.00	2.00	---	---	---	1.00	4.00
	SR	2.00	1.17	0.17	0.50	0.83	0.33	4.67
TATB	KJ	3.00	3.00	1.50	---	---	4.50	7.50
	KW	3.00	---	---	6.00	3.00	---	12.00
	mod-KW	3.00	3.00	---	3.00	---	3.00	9.00
	SR	3.00	1.00	1.00	3.00	2.00	2.00	10.00
Tetryl	KJ	2.50	2.50	2.75	---	---	4.25	7.75
	KW	2.50	1.00	---	7.00	1.50	---	12.00
	mod-KW	2.50	2.50	---	5.50	---	1.50	10.50
	SR	2.50	2.17	1.17	3.50	0.33	2.33	9.67

Compound	Rules	Moles of detonation products						Total moles of gaseous products, n
		$N_2(g)$	$H_2O(g)$	$CO_2(g)$	$CO(g)$	$H_2(g)$	$C(s)$	
DATB	KJ	2.50	2.50	1.75	---	---	4.25	6.75
	KW	2.50	---	---	6.00	2.50	---	11.00
	mod-KW	2.50	2.50	---	3.50	---	2.50	8.50
	SR	2.50	1.00	1.00	3.00	1.50	2.00	9.00
Picric acid	KJ	1.50	1.50	2.75	---	---	3.25	5.75
	KW	1.50	1.00	---	6.00	0.50	---	9.00
	mod-KW	1.50	1.50	---	5.50	---	0.50	8.50
	SR	1.50	1.50	1.00	3.50	---	1.50	7.50
Picramide	KJ	2.00	2.00	2.00	---	---	4.00	6.00
	KW	2.00	---	---	6.00	2.00	---	10.00
	mod-KW	2.00	2.00	---	4.00	---	2.00	8.00
	SR	2.00	1.00	1.00	3.00	1.00	2.00	8.00
TNB	KJ	1.50	1.50	2.25	---	---	3.75	5.25
	KW	1.50	---	---	6.00	1.50	---	9.00
	mod-KW	1.50	1.50	---	4.50	---	1.50	7.50
	SR	1.50	1.00	1.00	3.00	0.50	2.00	7.00
HNS	KJ	3.00	3.00	4.50	---	---	9.50	10.50
	KW	3.00	---	---	12.00	3.00	2.00	18.00
	mod-KW	3.00	3.00	---	9.00	---	5.00	15.00
	SR	3.00	2.00	2.00	6.00	1.00	6.00	14.00
TNT	KJ	1.50	2.50	1.75	---	---	5.25	5.75
	KW	1.50	---	---	6.00	2.50	1.00	10.00
	mod-KW	1.50	2.50	---	3.50	---	3.50	7.50
	SR	1.50	1.00	1.00	3.00	1.50	3.00	8.00

3   Calculation of Detonation Velocities and Detonation Pressures

The product compositions in Table 2 were used in conjunction with the experimental enthalpies of formation in Table 1 to calculate the quantities N, M_{ave} and Q that are required by Eqs. (1) and (2) in order to obtain D and P. The loading densities were as listed in Table 1. The enthalpies of formation of the products $N_2(g)$, $H_2(g)$ and $C(s)$ are zero; the ΔH_f° for $H_2O(g)$, $CO_2(g)$ and $CO(g)$ were taken from standard compilations of experimental data [15, 16]: -57.80, -94.05 and -26.42 kcal/mol, respectively.

In Table 3 are the values of $NM_{ave}^{0.5}$ and Q for each compound and each set of detonation products. For a given compound, these quantities can vary considerably for different sets of detonation products. The KJ rules give the highest Q and the lowest $NM_{ave}^{0.5}$. Both can be attributed to the KJ predicting the greatest amounts of CO_2, which has the most negative enthalpy of formation among the possible products (leading to a higher Q) but also uses up two oxygens, so that a larger portion of the molecular mass becomes solid carbon and N is smaller. The KW rules yield the lowest Q and highest $NM_{ave}^{0.5}$; they predict the least CO_2 and the most CO, and are also the greatest producers of H_2, which contributes nothing to Q but increases N.

Table 3. Calculated quantities for use in Eqs. (1) and (2) [a]

Compound	KJ		KW		mod-KW		SR	
	$NM_{ave}^{0.5}$	Q	$NM_{ave}^{0.5}$	Q	$NM_{ave}^{0.5}$	Q	$NM_{ave}^{0.5}$	Q
ε-CL-20	0.1719	1567	0.1850	1426	0.1850	1426	0.1807	1473
HMX	0.1762	1499	0.2013	1220	0.2013	1220	0.1930	1314
FOX-7	0.1762	1200	0.2013	921.1	0.2013	921.1	0.1930	1014
RDX	0.1762	1501	0.2013	1223	0.2013	1223	0.1930	1316
PETN	0.1744	1514	0.1865	1384	0.1865	1384	0.1825	1427
NQ	0.1844	911.9	0.2191	610.2	0.1844	911.9	0.2076	726.4
TATB	0.1515	1149	0.2156	544.9	0.1732	909.6	0.1874	826.1
Tetryl	0.1490	1438	0.2044	879.4	0.1851	1043	0.1743	1174
DATB	0.1481	1175	0.2127	555.6	0.1750	878.5	0.1827	854.2
Picric acid	0.1443	1280	0.1982	716.9	0.1901	785.4	0.1737	965.3
Picramide	0.1441	1255	0.2094	618.5	0.1771	893.8	0.1771	936.8
TNB	0.1394	1358	0.2055	702.0	0.1795	923.0	0.1707	1043
HNS	0.1319	1361	0.1946	740.1	0.1699	949.3	0.1616	1063
TNT	0.1352	1294	0.2042	631.4	0.1640	977.0	0.1721	951.0

[a] $NM_{ave}^{0.5}$ is in $(mole/g)^{0.5}$; Q is in cal/g.

Table 4 presents the detonation velocities D and detonation pressures P obtained with Eqs. (1) and (2), using the ρ in Table 1 and the $NM_{ave}^{0.5}$ and Q in Table 3. Several observations can immediately be made:

(1) In general, the results predicted by the different sets of rules are quite similar, despite the variation in $NM_{ave}^{0.5}$ and Q. The average range of D for each compound is 0.19 mm/μs, and for P it is 13 kbar.

(2) The Kamlet-Jacobs (KJ) D and P are usually the smallest in magnitude and also tend overall to be closest to the experimental values; this is indicated by the respective average absolute errors and the root-mean-square errors.

Table 4.   Calculated detonation velocities (D) and detonation pressures (P)

Compound	D, [mm/μs]					P, [kbar]				
	KJ	KW	mod-KW	SR	Exp.[a]	KJ	KW	mod-KW	SR	Exp.[a]
ε-CL-20	9.62	9.75	9.75	9.71	9.38[b]	441	453	453	450	---
HMX	9.15	9.29	9.29	9.27	9.10	384	395	395	393	393
FOX-7	8.63	8.63	8.63	8.66	8.869[c]	340	340	340	342	---
RDX	8.81	8.95	8.95	8.93	8.754	345	355	355	353	347
PETN	8.69	8.78	8.78	8.75	8.30	331	339	339	337	335
NQ	7.43	7.33	7.43	7.45	7.98	230	224	230	231	---
TATB	7.93	7.85	7.99	8.12	7.86	287	282	292	301	315
Tetryl	7.42	7.69	7.64	7.63	7.58[d]	228	245	241	241	226[d]
DATB	7.56	7.52	7.65	7.76	7.52	253	250	258	266	259
Picric acid	7.37	7.47	7.48	7.53	7.35[c]	232	239	240	243	---
Picramide	7.38	7.46	7.52	7.61	7.30[c]	235	240	244	250	---
TNB	7.17	7.38	7.39	7.43	7.27[d]	215	228	228	231	219[d]
HNS	7.27	7.58	7.54	7.56	7.13	230	250	247	249	---
TNT	6.98	7.17	7.16	7.29	6.95	204	215	215	222	190
Average absolute error	0.16	0.24	0.25	0.27		9	14	11	11	
Root-mean-square error	0.21	0.30	0.28	0.30		12	17	14	14	

[a]Experimental values are from Ref. 14 unless otherwise indicated.
[b]Ref. 33.
[c]Ref. 30.
[d]Ref. 1.

When the results are examined in relation to their oxygen balances, an interesting pattern emerges. For the compounds with the more positive OB, the different sets of rules tend to give more similar D and P than for those with more negative OB. For the six compounds with OB more positive than -31% (Table 1), the average D and P ranges are 0.11 mm/μs and 8 kbar; for the other eight they are 0.26 mm/μs and 17 kbar. This may reflect, at least in part, a common feature of the compounds with OB more positive than -31%: for each one, all four sets of rules predict that more than half of the moles of products are $N_2(g)$ and $H_2O(g)$.

However smaller ranges of predicted D do not lead to greater accuracy. Table 4 shows that the calculated detonation velocities of the first six compounds (which have the more positive OB) tend to deviate more from the experimental than do those of the other eight. For detonation pressures, on the other hand, the first six show the smaller deviations.

4 Discussion

For convenience, we will now follow the example of Kamlet and Jacobs and introduce the quantity φ [8], defined as,

$$\varphi = NM_{ave}^{0.5}Q^{0.5} \tag{4}$$

In terms of φ, Eqs. (1) and (2) take the form,

$$D \text{ (mm/}\mu\text{s)} = 1.01\varphi^{0.5}(1 + 1.30\rho) \tag{5}$$
$$P \text{ (kbar)} = 15.58\varphi\rho^2 \tag{6}$$

Table 4 has shown that, for a given compound and loading density, quite different proposed detonation product compositions tend to yield rather similar detonation velocities and pressures. In terms of Eqs. (5) and (6), this implies that φ is remaining approximately constant for each compound despite the changes in product compositions. Table 3 indicates that this is plausible, since $NM_{ave}^{0.5}$ and Q vary inversely, and Table 5 confirms it. The values of φ resulting from the different sets of rules vary relatively little for each compound individually. This feature of φ was noted earlier, on a more limited basis, by Kamlet and Ablard [34].

Table 5. Values of φ resulting from the different sets of rules [a]

Compound	KJ	KW	mod-KW	SR
ε-CL-20	6.80	6.99	6.99	6.93
HMX	6.82	7.03	7.03	6.99
FOX-7	6.10	6.11	6.11	6.15
RDX	6.82	7.04	7.04	7.00
PETN	6.79	6.94	6.94	6.89
NQ	5.57	5.41	5.57	5.60
TATB	5.14	5.03	5.22	5.39
Tetryl	5.65	6.06	5.98	5.97
DATB	5.08	5.01	5.19	5.34
Picric acid	5.16	5.31	5.33	5.40
Picramide	5.10	5.21	5.30	5.42
TNB	5.14	5.44	5.45	5.51
HNS	4.87	5.29	5.24	5.27
TNT	4.86	5.13	5.13	5.31

[a] Units of φ are (mol·cal)$^{0.5}$/g.

The reasons for this can be understood by extending earlier discussions [7, 13]. φ depends upon N, M_{ave} and Q, Eq. (4). N increases as more moles of the diatomic gases CO and H_2 are formed at the expense of the triatomic gases CO_2 and H_2O. However this decreases M_{ave} and also diminishes Q, since the enthalpies of formation of CO(g) (-26.42 kcal/mol) and H_2(g) (zero) are much less negative than those of CO_2(g) (-94.05 kcal/mol) and H_2O(g) (-57.80 kcal/mol) [15, 16]. Since φ contains N to a higher power than M_{ave} and Q, Eq. (4), these effects essentially balance in determining φ.

It has long been known that, for a given compound, the detonation velocity and pressure can be related to the loading density alone, at least for a specified range of ρ [3, 11, 14, 35, 36]:

$$D \sim \rho \tag{7}$$
$$P \sim \rho^2 \tag{8}$$

Table 6.   Properties at two different loading densities [a]

Moles of products per mole explosive[b]	RDX, **1**		PETN, **3**		TNT	
	$\rho = 1.80$	$\rho = 1.0$	$\rho = 1.77$	$\rho = 0.50$	$\rho = 1.64$	$\rho = 0.732$
N_2(g)	3.00	2.98	2.00	1.93	1.50	1.49
H_2O(g)	3.00	2.80	4.00	3.73	2.50	1.76
CO_2(g)	1.49	0.67	3.89	2.81	1.66	0.69
CO(g)	0.022	1.855	0.223	2.188	0.188	2.865
H_2(g)	---	0.111	---	0.167	---	0.707
O_2(g)	---	---	---	0.072	---	---
NH_3(g)	---	0.029	---	0.001	0.001	0.020
CH_4(g)	---	0.021	---	---	---	---
NO(g)	---	---	---	0.134	---	---
C(s)	1.49	0.45	0.89	0.0	5.15	3.45
Calculated properties						
$NM_{ave}^{0.5}$	0.1763	0.1929	0.1758	00.1868	0.1369	0.1646
Q^c	1499	1321	1500	1285	1279	1001
φ	6.83	7.01	6.81	6.70	4.90	5.21

[a] Units: ρ, g/cm^3; N, moles/g; M_{ave}, g/mol; Q, cal/g.
[b] BKW code, Ref. 14.
[c] Enthalpies of formation of RDX, PETN and TNT are given in Table 1. Those of the products were taken from Refs. 15 and 16.

These relationships, in themselves, may appear to be inconsistent with the fact that changing ρ affects the detonation product composition and hence N, M_{ave}

and Q – upon which, along with ρ, D and P depend. However the dependence of D and P upon N, M_{ave} and Q is only through φ – Eqs. (5) and (6) – and Table 5 shows φ to be roughly constant for different product compositions. When this is taken into account, Eqs. (5) and (6) yield Eqs. (7) and (8).

To illustrate explicitly that different densities have relatively little effect upon φ, Table 6 gives the detonation products at high and low loading densities of three of the explosives in Tables 1-5. The data were generated by the BKW code [14]. Table 6 also includes the values of $NM_{ave}^{0.5}$, Q and φ.

The data in Table 6 are fully consistent with the earlier statements that the primary detonation products are $N_2(g)$, $H_2O(g)$, $CO_2(g)$, $CO(g)$, $H_2(g)$ and $C(s)$. The main consequence of going to lower loading densities is to considerably increase the amount of CO, and to a lesser extent the H_2; the H_2O and CO_2 decrease. As discussed above, this results in higher $NM_{ave}^{0.5}$ but lower Q; however the net effects upon φ are small (between 1.6% and 6.3%) despite large changes in density (between 44% and 72%). Thus Table 6, in conjunction with Eqs. (5) and (6), demonstrates the basis for Eqs. (7) and (8).

5   Summary

Due to a partial balancing of opposing effects, the four procedures for predicting detonation product composition generally lead to quite similar results for the detonation velocity D and the detonation pressure P, for a particular compound and loading density. The Kamlet-Jacobs values are, on average, closest to the experimental. For analogous reasons, D and P can be correlated to some extent with just loading density, despite the changes in detonation products that are known to accompany variations in density.

We want to emphasize, however, that while the differences in the detonation product compositions that have been investigated have relatively little effect upon D and P, this is not necessarily true of other properties. Tables 2, 3 and 6 show that the number of moles of gaseous products n (and accordingly their volume), the quantity $NM_{ave}^{0.5}$ and the heat release Q can vary considerably with product composition. Thus, for example, while the detonation products predicted by the Kamlet-Jacobs rules lead to generally good results for D and P, the corresponding Q can be significantly less accurate [26, 34, 37].

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