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Calculating the heat of explosion for non-ideal explosives

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Non-ideal explosives are typically highly porous, low-density heterogeneous materials. They differ from ideal explosives in that fuel and oxidiser are separated at the molecular level. As such, non-ideal explosives demonstrate lower detonation pressures and velocities than ideal explosives, with more extended detonation reaction zones. These longer detonation reaction zones produce higher heat of explosion due to secondary and tertiary combustion reactions occurring behind the detonation front. Non-ideal explosives are increasingly used as homemade explosives (HME), and it is often challenging to determine likely performance without detailed chemical analysis, or an understanding of loading density, critical diameter, and stoichiometry. Detailed analysis is not an option in security-related settings where preservation of life and property is often challenged by time. Using Hess' Law of enthalpy, and empirical and quantitative thermochemical methods to determine the products of detonation, this paper introduces a simple method to determine the heat of explosion of any non-ideal explosive composition during three specific stages: anoxic detonation; anaerobic combustion; and aerobic combustion. The values calculated compare favourably to heats of explosion for non-ideal explosives published in open-source literature, suggesting that the approach can be developed into a user-friendly application for first responders.

1 Introduction

In the decade preceding COVID-19, non-ideal explosives were used in 43% of deliberate acts of explosive violence in Europe,[1] with the United Kingdom, France, and Spain having accounted for over 65% of such attacks.[2] Identification of explosive chemical precursors (ECP), which may be incorporated within an improvised explosive device (IED), can be hugely problematic for first responders and the public.[3] The choice of ECP available to criminals is broad, given the limited regulation applied to some energetic compounds.[4] As such, first responders across the international arena may be required to apply rapid judgement on the explosive performance of HME compositions. This is because of the overriding philosophy to preserve life, preserve property and return situations to normality within sensible timeframes.[5, 6] Judgement has been based on the knowledge of more conventional homogeneous explosives, not the heterogeneous nature of criminal compositions, with evacuation distance based on a bare charge mass equivalent of TNT.[7, 8]

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However, many non-ideal explosive compositions, particularly those based on nitrate esters, can be much more powerful than TNT[9, 10] and are relatively simple to synthesise,[11, 12] suggesting that greater refinement of safety distance may be necessary.[13, 14]

Whilst media attention has often focused on typical non-ideal explosive compositions comprising ammonium nitrate (AN), regulation has improved considerably for the most frequent HME encountered.[15] However, as supply chains become more heavily regulated, other fuels and oxidisers, or multiple mixtures of fuels and oxidisers, will be selected out of necessity and availability – this is simply the economics of supply and demand.[16] This trajectory has already been witnessed in Afghanistan, where regulation of ammonium nitrate led to the prolific use of potassium chlorate.[17]

Therefore, such compositions must be assessed quickly and effectively at the point of discovery based on available information. This information could come from intelligence provided to the first responder, on the chemical labels visible at the crime scene, on the physical appearance of partly synthesised or final product, the results of rapid chemical testing (if accessible), witness testimony, or affirmation from technical experts should they be available. The authors conclude that several *'ifs'* face a first responder in what can only be described as a particularly challenging environment when timely decision-making is required.

Zeldovich,[18] von Neumann,[19] and Doering[20] (ZND) explicitly described a one-dimensional detonation model for ideal explosives, comprising a leading shock front followed by a chemical reaction zone. For ideal explosives, all the potential energy contained within the explosive is released almost instantly in a short reaction zone,[21, 22] with the typical ZND model describing the following:

- a vertical shock front (with associated ignition temperature (T_i), detonation pressure (D_p) and density (ρ_o)) within a *CHNO* explosive undergoing detonation;
- induction/reaction zones (where the dissociated molecules of the explosive form the principal products of detonation[23]); and
- a non-driving reaction zone where the products of detonation react with other species.

In this latter non-driving reaction zone, most additives to *CHNO* compositions compete with the gaseous detonation products to increase the heat of explosion *(Q_e)* and alter the volume of gaseous products produced.[24] The heat of explosion is therefore driven by the enthalpies of formation of the explosive products *($CO_{(g)}$, $CO_{2(g)}$, $H_2O_{(g)}$, $NO_{2(g)}$ etc)* dependent upon explosive composition, oxygen balance and stoichiometry. There is an order of precedence as to which products are formed first.[25]

In current literature, the performance of ideal explosives comprising *CHNO* can be determined through the application of empirical and quantitative thermochemical methods published by Kamlet-Jacobs,[26] Kistiakowsky-Wilson,

Springall-Roberts,[27] and Cooper.[21] Consideration has also been given to the performance of conventional explosives enhanced with highly reactive atoms such as chlorine, fluorine and aluminium,[28] which are therefore non-ideal explosives by definition.

In contrast to the ZND model, non-ideal explosives can be considered to have multiple reaction zones behind the detonation shock front, as shown in Figure 1, which influence performance. The line *AB* depicts the detonation shock front, with *CD* the point at which reactants are converted to products. The sonic locus depicts the region of the detonation driving zone where energy is released to sustain the shock front. Scott-Stewart and Kasimov[29] describe the sonic locus as an exact balance of heat release (*Q*) and flow divergence. The flow speed behind this region is sonic relative to the shock front and is therefore part of the non-driving reaction zone. As such, energy release is slower, detonation pressures lower, with a lack in oxygen balance being a contributory factor.

[Insert Figure 1 here]

For example, in the case of a *CHNO* explosive such as *TNT* and *RDX*, the detonation velocity is typically proportional to the heat of explosion *(Q)*, meaning that the higher the value of *Q*, the greater the detonation velocity.[21, 23, 30] However, this is not true for non-ideal explosives. Adding aluminium powder increases the heat of explosion,[31] which is dominated by mass diffusion and conduction.[32] At the same time, the detonation velocity is decreased because of the endothermic effect of the aluminium powder during the primary reaction stage.[33]

As such, the addition of aluminium generates high thermal loading[34] and produces an extended pressure pulse[35] when it reacts with the gaseous detonation products. The smaller the particle size (increasing surface area) and the nearer the approach to stoichiometry (the proportions where elements or compounds react fully with one another), the higher the heat of explosion.[36] However, if too much fuel is added, as can often be the case with HME, or the particle size of the additive is too large, this detracts significantly from the detonation velocity to the extent that detonation may not occur at all.[24, 37]

As such, one would expect non-ideal explosives comprising finely powdered fuels or metal flakes, and oxidisers with excess oxygen, to have a lower detonation velocity than their homogeneous counterparts,[29] but release significant energy upon detonation in a three-stage process outlined below (see Table 1).

[Insert Table 1 here]

The energy release in Stages 1 and 2 represent the amount of energy available for the explosive to perform mechanical work on the surroundings, whilst Stage 3 contributes to additional thermal energy that the explosive could deliver over a period of milliseconds (excess fuel and atmospheric oxygen dependent). Therefore, substance identification and an understanding of energy release are significant to the first responder, not least because of the mechanical work that

the explosive can inflict on the surroundings (such as blast overpressure, impulse and fragmentation) but also because of potential thermobaric injuries caused during the aerobic combustion phase.

2 Method

This paper reviews open-source approaches used to determine the oxygen balance and heat of explosion of ideal and non-ideal explosive compositions. It has sought clarification from organisations such as Fraunhofer Institute for Chemical Technology (ICT) to determine that existing modelling tools do not establish the detonation products for multiple HME formulations.[46]

Based on the methods devised by Kistiakowsky-Wilson, Springall-Roberts, Kamlet-Jacobs, Keshavarz and Cooper,[21, 25 - 27] this paper offers a generic chemical equation to predict the heat of explosion (Q_e) and TNT equivalence (*TNTe*) for any non-ideal explosive that may take the form of Equation 1:

$$C_aH_bN_cO_dLi_{li}Na_{na}K_kMg_{mg}Ba_{ba}Zn_{zn}B_bAl_{al}Pb_{pb}F_fCl_{cl}S_sSr_{sr}Br_{br}I_i \quad (1)$$

This equation considers not only current HME formulations where regulation is applied,[44] but also those formulations that may be devised as supply chains become constrained.[13, 14, 47] Typical compositions could, therefore, contain any number of the fuels and oxidisers.

TNTe has been chosen as the comparator, given its doctrinal use in energetic performance on land[48] and at sea[49] for over a century. However, it is acknowledged that *TNTe* for high and low explosives depends on the measurement method, and errors exceeding 30% are typical.[50] This is a significant margin for the first responder in terms of blast, fragmentation, safety distance, or indeed the thermal energy available to inflict quaternary physical injury.[45] For example, the values of *TNTe* for ideal and non-ideal explosives identified by the ballistic mortar test[51] are entirely different to that proposed by other methods such as peak overpressure/positive impulse[52] and the lead block test.[53] As such, it is essential to standardise the measurement by which any calculator operates, and base measurement upon theoretical and/or experimental literature findings. For this paper, the reference used is the heat of explosion under constant volume conditions *(Q_v)* where data for some non-ideal compositions in kJ kg^{-1} can be found for Stage 1 and 2 reactions.[10, 54, 55] A comparison of Q_e (the heat of explosion calculated for those Stage 1 and 2 reactions) is then conducted against Q_v (the reference value) to determine accuracy. This paper does not calculate the potential thermal energy from any Stage 3 reaction since it does not contribute to the mechanical work available to the explosion products.[37]

TNTe for each explosive is then calculated as follows (see equation 2), with Q_{tnt} taken as 4091.6 kJ kg^{-1} from literature:[27]

$$TNT_e(kJkg^{-1}) = \left(\frac{Q_e}{Q_{tnt}}\right) \quad (2)$$

A 4-step process is then applied to the methodology, as can be seen in Table 2, with worked examples to underpin the theory at Appendices:

[Insert Table 2 here]

3 Assumptions

Several assumptions underpin calculations given the complexity of thermochemical reactions during detonation and combustion. Table 3 outlines these assumptions to provide a simplistic baseline for the proof of concept.

[Insert Table 3 here]

Enthalpies of formation used for calculation are listed in Table 4. Unless stated otherwise, all enthalpies are provided to one decimal place. These enthalpies measure the relative thermochemical stabilities of the molecules, intimately related to their structures. For example, carbon dioxide displays greater thermal stability than carbon monoxide, and aluminium oxide displays greater thermal stability than barium oxide. Values for Q_e and Q_v are presented as kJ kg^{-1} and kJ mol^{-1}.

[Insert Table 4 here]

4 Results and Discussion

4.1 Derivation of baseline programme in Excel to determine oxygen balance and heat of explosion– STEP 1

The equation for a $C_aH_bN_cO_d$ explosive oxygen balance can be seen in Equation 3, which is widely published in literature.[27] The letters in subscript *(a, b, c,* and *d)* refer to the total number of atoms of carbon, hydrogen, nitrogen and oxygen in each explosive molecule. The contribution of nitrogen *(c)* to the oxygen balance is zero, since nitrogen does not bind to the other elements, and is therefore absent from calculation:

$$\Omega = 15.999 \times \frac{(d - 2a - {}^{b}/_{2})}{molecular\ weight} \times 100\% \quad (3)$$

Considering Equation 1, many fuels can be added to a *CHNO* explosive, such as *Al, B, Ba, Ca, Cl, F, K, Li, Mg, Mn, Na, Pb, Hg, S* and *Zn*. Each will behave in its own unique fashion. To determine the oxygen balance for such non-ideal compositions, the following principles of chemistry are considered, based on the oxidation-reduction reactions described in Table 1 and the enthalpies of formation that accompany the reactions ($(\triangle H_f)$ in kJ mol^{-1}):

1. Since *C* is oxidised to CO_2, each *C* atom requires 2O = 2a: $\triangle H_f$ -393.5
2. Since *H* is oxidised to H_2O, each *H* requires O/2 = b/2: $\triangle H_f$ -241.8

3. Since *N* goes to N_2, there is no need of oxygen = c x 0 = 0: $\triangle H_f$ = 0.0
4. Since *Al* oxidises to Al_2O_3, each *Al* requires 3O/2 = 3Al/2: $\triangle H_f$ = -1669.8
5. Since *B* oxidises to B_2O_3, the same argument for *Al* applies 3B/2: $\triangle H_f$ = -1263.6
6. Since *Ca* oxidises to CaO, each Ca requires one O = Ca - $\triangle H_f$ = -635.5
7. Since *Mg* oxidises to *MgO*, each *Mg* requires one O = Mg: $\triangle H_f$ = -601.8
8. Since *Na* oxidises to Na_2O, each *Na* requires 0.5O = Na/2: = -416.0
9. Since *K* oxidises to K_2O, each *K* required 0.5O = K/2: $\triangle H_f$ = -363.2
10. Since *Zn* oxidises to *ZnO*, each *Zn* requires one O = Zn: $\triangle H_f$ = -348.0
11. Since *S* oxidises to SO_2, each *S* requires 2 O = 2S: $\triangle H_f$ = -296.1
12. Since the oxidation number for *H* and *F* are +/1 respectively, each *F* requires one *H*, thereby reducing H_2/H_2O by 0.5 = -F/2: $\triangle H_f$ = -286.6
13. Since the oxidation number for *H* and *Cl* are +/1 respectively, each *Cl* requires one *H*, thereby reducing H_2/H_2O by 0.5 = -Cl/2: $\triangle H_f$ = -92.3
14. Since the oxidation numbers of *H* and *Br* are +/1 respectively, each *Br* requires one *H*, thereby reducing H_2/H_2O by 0.5 = -Br/2: $\triangle H_f$ = -36.2
15. Since the oxidation numbers of *H* and *I* are +/1 respectively, each *I* requires one *H*, thereby reducing H_2/H_2O by 0.5 = -I/2: $\triangle H_f$ = +26.5

This approach is consistent with thermochemical code methodologies used to predict the detonation velocity of organic, inorganic and mixed explosives, whereby the more reactive elements of the explosive compound (those with the higher enthalpies) react first, and form detonation products based on the hierarchy of the heats of reaction.[25]

The establishment of the baseline programme in excel from these principles was based on the manipulation of explosive compositions within Equation 3, using the appropriate Kistiakowsky-Wilson conditions. This step is not shown, as examples of calculations using Equation 3 are widely published.[27] The next step is to derive the oxygen balance formula for non-ideal explosives.

4.2 Derivation of non-ideal oxygen balance formula – STEP 2

From recent research at Cranfield University,[4] only certain ECPs are considered for HME manufacture, and predictive analysis can determine future trends.[64] As such, Equation 1 constitutes the principal fuel and oxidiser compositions that could be readily encountered within geographical supply chains. The products of detonation and combustion depend very much on the oxygen balance of the explosive composition and the Kistiakowsky-Wilson and modified Kistiakowsky-Wilson conditions. It is, therefore, important to understand the role

of constituent atoms within the explosive molecule during anoxic detonation and anaerobic combustion. The following examples are provided to demonstrate the effect of oxygen balance within an explosive as detonation occurs, using known explosive compositions to derive the formula.

4.2.1 Example 1 - When the explosive is hugely oxygen deficient

When the amount of oxygen within the explosive molecule $C_aH_bN_cO_d$ is much less than carbon ($d \leq a, or\ O \leq C$), then $C_{(s)}$ will dominate the products of detonation, dependent upon the oxidation reactions between $CO_{(g)}$ and $H_{2(g)}$:

$$\therefore explosion\ products \rightarrow \frac{c}{2}N_2 + dCO + (a-d)C + (\frac{b}{2})H_2 \quad (4)$$

To determine if this is correct, consider the liquid explosive 3-nitro-toluene *(3-NT)*, with molecular structure $C_7H_7NO_{2(l)}$. Using Equation 3, *3-NT* has an oxygen balance of:

$$\Omega = 15.999 \times \frac{(d-2a-{}^{b}/_{2})}{molecular\ weight} \times 100\% \quad (5)$$

$$\therefore \Omega = 15.999 \times \frac{(2-14-3.5)}{137.14} \times 100\% \quad (6)$$

$$\therefore \Omega = -180.8\%$$

3-NT would require 8.75 additional $O_{2(g)}$ to form $CO_{2(g)}$ and $H_2O_{(g)}$, which means it is hugely oxygen deficient (-181%).[56] Using the Kistiakowsky-Wilson rules,[27] the products of detonation for an ideal explosive using Equation 4 would be as follows, which is consistent with literature:[65]

$$\therefore C_7H_7NO_{2(l)} \rightarrow \frac{1}{2}N_2 + 2CO + (7-2)C + (\frac{7}{2})H_2 \quad (7a)$$

$$\therefore C_7H_7NO_{2(l)} \rightarrow 0.5\ N_{2(g)} + 2\ CO_{(g)} + 5\ C_{(s)} + 3.5\ H_{2(g)} \quad (7b)$$

However, if those atoms in Group 7 of the Periodic Table with a valance of -1 were introduced to *3-NT* (such as *F, Cl, Br,* and *I*) then, based on the assumptions in Table 3, these atoms would naturally compete with hydrogen in the detonation reaction zone[25] and the products would become:

$$\frac{c}{2}N_2 + fHF + clHCl + brHBr + iHI + dCO + (a-d)C + (\frac{b-f-cl-br-i}{2})H_2 \quad (8)$$

Note: *a, b, c, d, f, cl, br* and *i* denote the number of atoms present within the molecular formula for explosive $C_aH_bN_cO_dF_fCl_{cl}Br_{br}I_i$; all molecular weights from the periodic table are shown to two decimal places.

4.2.2 Example 2 - When the amount of oxygen exceeds that of carbon

When the amount of oxygen exceeds that of carbon, but the explosive remains oxygen deficient, then there will be insufficient oxygen to go beyond the formation of carbon monoxide and water. The following condition describes this relationship:

$$O > CO \; and \; H_2O > O - CO \; (9a)$$

$$\therefore d > a \; and \; \left(\frac{b - f - cl - br - i}{2}\right) > d - a \quad (9b)$$

To determine if this is correct, consider *RDX*, with the molecular formula $C_3H_6N_6O_{6(s)}$. The detonation products favour a less negative oxygen balance than *3-NT* (-21.6%). As such, the products of detonation take the following form, which is consistent with literature and the Kistiakowsky-Wilson rules:[27]

$$\frac{c}{2}N_2 + aCO + (d-a)H_2O + \left(\frac{b}{2} - (d-a)\right)H_2 \qquad (10a)$$

$$\therefore \frac{6}{2}N_2 + 3CO + (6-3)H_2O + \left(\frac{6}{2} - (6-3)\right)H_2 \qquad (10b)$$

$$\therefore C_3H_6N_6O_{6(s)} \rightarrow 3N_{2(g)} + 3CO_{(g)} + 3H_2O_{(g)} \qquad (10c)$$

If those atoms in Group 7 of the Periodic Table with a valance of -1 were to be added to *RDX* (such as *F, Cl, Br,* and *I*), thereby creating non-ideal conditions, then these atoms would naturally compete with hydrogen and the detonation products would become:

$$\frac{c}{2}N_2 + fHF + clHCl + brHBr + iHI + aCO + (d-a)H_2O + \left(\frac{b-f-cl-br-i}{2} - (d-a)\right)H_2 \qquad (11)$$

4.2.3. Example 3 - When the explosive oxygen balance tends towards zero

In the situation where oxygen remains more than that required to compete in the formation of carbon monoxide and the products of hydrogen (such as H_2O and *HF* etc), but there is no excess of oxygen in the post-reaction phase, then carbon monoxide will oxidise to carbon dioxide. Such conditions are met when:

$$O \geq CO + H_2O \; but \; O \leq CO_2 + H_2O \qquad (12)$$

$$\therefore d \geq a + \left(\frac{b-f-cl-br-i}{2}\right) \; but \; d \leq 2a + \left(\frac{b-f-cl-br-i}{2}\right) \qquad (13)$$

The oxygen balance becomes even less negative and tends towards zero, where the Kistiakowsky-Wilson rules dictate an ever-increasing presence of $CO_{(g)}$, $H_2O_{(g)}$ and $CO_{2(g)}$.

To determine if this is correct, consider *PETN* with the molecular formula $C_5H_8N_4O_{12(s)}$ (oxygen balance -10%). The products of detonation can be determined as follows, which equates well with literature:[25, 27]

$$\frac{c}{2}N_2 + \left(\frac{b}{2}\right)H_2O + \left(a - \left(d - a - \frac{b}{2}\right)\right)CO + \left(d - a - \frac{b}{2}\right)CO_2 \qquad (14a)$$

$$\therefore \frac{4}{2}N_2 + \left(\frac{8}{2}\right)H_2O + \left(5 - \left(12 - 5 - \frac{8}{2}\right)\right)CO + \left(12 - 5 - \frac{8}{2}\right)CO_2 \qquad (14b)$$

$$\therefore C_5H_8N_4O_{12(s)} \rightarrow 2N_{2(g)} + 4H_2O_{(g)} + 2CO_{(g)} + 3CO_{2(g)} \qquad (14c)$$

If those atoms in Group 7 of the Periodic Table with a valance of -1 were to be added to *PETN* (such as *F, Cl, Br*, and *I*), then these atoms would naturally compete with hydrogen and the detonation products would become:

$$\frac{c}{2}N_2 + fHF + clHCl + brHBr + iHI + \left(\frac{b-f-cl-br-i}{2}\right)H_2O + \left(2a - d + \frac{b-f-cl-br-i}{2}\right)CO + \left(d - a - \frac{b-f-cl-br-i}{2}\right)CO_2 \qquad (15)$$

4.2.4. Example 4 - When an oxygen surplus is evident within the explosive

In a situation where there is an abundance of oxygen in the explosive, such as nitroglycerine *NG* ($C_3H_5N_3O_{9(l)}$), then unused oxygen remains after the production of carbon dioxide and water. This is described by the condition:

$$O > CO_2 + H_2O \qquad (16a)$$

$$\therefore d > 2a + \left(\frac{b-f-cl-br-i}{2}\right) \qquad (16b)$$

The products of detonation would comprise $O_{2(g)}$, $H_2O_{(g)}$ and $CO_{2(g)}$ as follows:[27]

$$\frac{c}{2}N_2 + \left(\frac{b}{2}\right)H_2O + aCO_2 + \left(\frac{d - \frac{b}{2} - 2a}{2}\right)O_2 \qquad (17a)$$

$$\therefore C_3H_5N_3O_{9(l)} \rightarrow \frac{3}{2}N_2 + \left(\frac{5}{2}\right)H_2O + 3CO_2 + \left(\frac{9 - \frac{5}{2} - 6}{2}\right)O_2 \qquad (17b)$$

$$\therefore C_3H_5N_3O_{9(l)} \rightarrow \frac{3}{2}N_{2(g)} + 2\frac{1}{2}H_2O_{(g)} + 3CO_{2(g)} + \left(\frac{1}{4}\right)O_{2(g)} \qquad (17c)$$

If those atoms in Group 7 of the Periodic Table with a valance of -1 were to be added to *NG* (such as *F, Cl, Br,* and *I*), then these atoms would naturally compete with hydrogen and the detonation products would become:

$$\frac{c}{2}N_2 + fHF + clCl + brBr + iI + \left(\frac{b-f-cl-br-i}{2}\right)H_2O + aCO_2 + \left(\frac{2d-b+f+cl+br+i}{4} - a\right)O_2 \qquad (18)$$

Therefore, the valance of atoms in a non-ideal explosive containing some, or all the atoms annotated in Equation 1 can determine the overall products of detonation for a non-ideal explosive. The above process can be repeated for atoms within each Group of the Periodic Table, and mixtures containing atoms across multiple Groups.

4.2.5 Derivation of overall oxygen balance for a non-ideal explosive

Examples 1 – 4 demonstrate the impact of Group 7 atoms on oxygen balance and products of detonation for ideal explosives. A similar situation applies to Groups 1 – 6, as shown in Table 5:

[Insert Table 5 here]

As such, the basic oxygen balance equation for an ideal explosive (Equation 3) can be refined according to the atomic composition of *O, C, H, N, Li, Na, K, F, Cl, Mg, Ba, Zn, Al, B, Pb, Sr, Br, I* as follows:

$$\therefore \Omega = 15.999 \times \left(\frac{d - 2a - \frac{b}{2} - \frac{Li}{2} - \frac{Na}{2} - \frac{K}{2} + \frac{F}{2} + \frac{Cl}{2} + \frac{Br}{2} + \frac{I}{2} - Mg - Ba - Zn - Sr - \frac{3Al}{2} - \frac{3B}{2} - 2Pb}{molecular\ weight} \right) \times 100. \quad (19)$$

This then provides the generic formula for oxygen balance for HME compositions as follows:

$$\therefore \Omega = \frac{15.999\left(d - 2a - \frac{b}{2} + (2\sum Valence(\pm 4) + {}^{3}/_{2}\sum Valence(\pm 3) + \sum Valence(\pm 2) + {}^{1}/_{2}\sum Valence(\pm 1) + \cdots)\right)}{molecular\ weight} \times 100 \quad (20)$$

Note: *F, Cl, Br* and *I* atoms are positive values in the equation above since they compete with the hydrogen in water, thereby releasing oxygen from the water. Atoms such as *C, H, Mg, Li, Na* and *Al* attract a negative value in the equation because they compete for oxygen within the molecule.

4.2.6 Example 5 – Determining the detonation products for bisflourodinitroethyl formal (FEFO) and PBX 9407 (94/6 RDX/Exon 461)

In this example, *Cl* and *F* are introduced to the composition of a *CHNO* explosive. Detailed calculations can be found in Appendix A, with only the results highlighted in the main text.

Consider *FEFO* with the molecular formula $C_5H_6N_4O_{10}F_{2(l)}$ and molecular weight 320.12 g. As the explosive is non-ideal, theory dictates that Equation 19, not Equation 3, should be considered to determine oxygen balance. This equation calculates the oxygen balance for FEFO to be -9.99%

The following products of detonation can then be determined from Example 3 (Equation 14a), where the conditions for a slightly negative oxygen balance are established:

$$\therefore C_5H_6N_4O_{10}F_{2(l)} \rightarrow 2N_{2(g)} + 2HF_{(g)} + 2H_2O_{(g)} + 2CO_{(g)} + 3CO_{2(g)} \quad (21)$$

The oxygen balance and products of detonation support reported literature values.[57]

Consider PBX 9407 with molecular formula $C_{1.41}H_{2.66}N_{2.54}O_{2.69}Cl_{0.07}F_{0.09(s)}$ and molecular weight 102.42 g.[28] Again, the explosive is non-ideal. One would therefore anticipate the oxygen balance and products of detonation to be based on Equations 14 and 19. Calculations at **Appendix A** realise an oxygen balance of -21.58%, with the following products of detonation determined:

$$\therefore C_{1.41}H_{2.66}N_{2.54}O_{2.69}Cl_{0.07}F_{0.09(s)} \rightarrow 1.27N_{2(g)} + 0.09HF_{(g)} + 0.07HCl_{(g)} + 1.25H_2O_{(g)} + 1.38CO_{(g)} + 0.03CO_{2(g)} \quad (22)$$

4.3 Comparison of homogeneous and binary compositions, with Q calculated from Hess' Law – STEP 3

Using Equation 1 and Equation 19, Table 6 provides the calculated values of oxygen balance (Ω) and heat of explosion (Q_e) for ideal and binary non-ideal explosives compositions. These are compared with published literature values of heat of explosion at constant volume (Q_v).

AN/Al (88/12) is provided as the worked example at **Appendix B**.

AN/Al (88/12) is a composition with a positive oxygen balance of +6.92%.[55] As such, it should follow the process described in example 3 where a CHNO explosive would tend towards the formation of $N_{2(g)}$, $O_{2(g)}$, $H_2O_{(g)}$ and $CO_{2(g)}$. However, in this example, there is no carbon present so the products of detonation would tend towards $N_{2(g)}$, $H_2O_{(g)}$ and $Al_2O_{3(s)}$. The empirical formula by molar quantities within 1g is therefore determined from calculation at Appendix B as:

$$H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447(s)} \quad (23)$$

Following the stages and assumptions described in Table 3, the aluminium competes with the detonation products formed, in this case H_2O(g), and any excess oxygen remaining after the formation of the detonation products. The heat of explosion for this reaction is then determined from Hess' Law (see Equation 24), with enthalpy values taken from Table 4:

$$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f(products)} - \sum \Delta H^{\theta}_{f(reactants)} \quad (24)$$

The total heat of explosion produced during this process is shown in Table 7, along with the products of detonation at each stage:

[Insert Table 6 here]

[Insert Table 7 here]

From these results the calculator determines the accuracy for *AN/Al (88/12)* as 101.8% against the heat of explosion (Q_v) reported in literature.

4.4 Comparison of HME compositions comprising more complex mixtures, with Q calculated from Hess' Law – STEP 4

Following success of the valence formula with simple compositions, more complex interactions were interrogated against open-source literature values for Q_v. The example used in the calculation is Baronal, a ternary mixture comprising barium nitrate, TNT, and Al (50/35/25).

Calculations at **Appendix C** identify the molecular formula for this non-ideal explosive to be:

$$C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556(s)} \quad (25)$$

As such, the oxygen balance for Baronal can be determined as -23.92% using Equation 19. There is, therefore, insufficient oxygen to produce $CO_{2(g)}$ and $H_2O_{(g)}$ during anoxic detonation (Stage 1). And, since barium and aluminium are inert *'passengers'* during that initial stage, they become major liberators of heat in the formation of their metal oxides during the anaerobic stage (Stage 2). Therefore, the products of detonation and heat of explosion can be determined from Equation 14 as (see Table 8):

[Insert Table 8 here]

Table 9 shows the results obtained for seven further published non-ideal compositions and one lead-based composition (lead azide), which carries no oxygen within its molecular structure. A simple shading system depicts Q_e lying within 10% Q_v (none), and those lying within 20% (grey). The common name for each explosive is annotated where known.

[Insert Table 9 here]

Table 10 provides further calculation relating to 3 non-ideal compositions encountered by first responders,[1] where literature reference on performance is not readily available. Whilst these results are merely speculative, they suggest that the calculator can provide rapid determination of HME performance in a security-related setting. The common names for compositions are annotated where known.

[Insert Table 10 here]

The values of Q_e obtained from the valence formula in Table 9 present a *'worst case'* situation for the first responder and differ (in some instances) from literature due to the enthalpies of formation chosen for the more complex hydrocarbons such as fuel oil, woodmeal, vaseline and paraffin wax. These values were scarcely found, yet are necessary for the critical evaluation of data. For example, if the formula for fuel oil is taken as $C_{18}H_{38(l)}$, then the enthalpy of formation for this hydrocarbon (–378 kJ mol^{-1})[70] improves the accuracy of *ANFO/Al* calculations to 104%.

Additionally, barium is understood to continue energetic reactions well behind the shock front, where only a percentage of its oxygens react with carbon.[71] As such, it is reasonable to determine that experimental literature values for Baronal

and Baratol may always be lower than those calculated in these examples since the equation of state considers optimum conditions.

Loading density, critical diameter, porosity, particle size, confinement and homogeneity of oxidiser/fuel mix, are also of huge importance in any effective calculation of explosive performance, since each aspect plays a role in the deflagration to detonation (DDT) transition.[29] For example, if density and critical diameter are below certain values for any explosive, then DDT cannot progress.[72]

However, some explosive compositions can behave in a unique fashion. For example, TNT compositions may experience decreasing critical diameters with increasing density (and increasing detonation velocity with loading density), whilst others such as ammonium nitrate may exhibit the opposite effects.[73] Therefore, focusing on the thermochemistry within this model mitigates significant 'unknowns' associated with HME manufacture, thereby calculating the worst-case conditions for the first responder. It removes the complexity of Chapman-Jouget detonation pressures and simplifies the thermochemistry behind driving and non-driving detonation reaction zones. Indeed, if the complexity of detonation velocity (D) were required, then perhaps it could be predicted from the Q_e values obtained in Stages 1 and 2 of the detonation process, and using the equation of state for D and Q proposed by Kamlet-Jacobs[26] and Cooper.[21]

Finally, the standard enthalpy of formation is a key parameter in thermochemistry. The precision of calculations could be improved using a rotating bomb calorimeter for the types of fuels used in non-ideal explosive compositions. Examples of this would be ground coffee (used in the 7/7 bombings in London[74]) or the type of diesel commonly found in fuel stations. However, combustion calorimetry is hugely difficult to conduct since the precision in experimentation needs to be ± 0.01-0.02% to have an uncertainty in an enthalpy of formation[75] of ± 1 $kJmol^{-1}$. Additionally, non-ideal compositions containing sulphur or halogens would require specific testing conditions given the highly erosive nature of the gaseous products. Therefore, it may be prudent to consider those fuels with the lower enthalpy values if the precise detail of the hydrocarbon (for example) cannot be determined.

5 Conclusion

The heat of explosion of non-ideal explosives has been historically difficult to model due to the significant departure of highly non-ideal detonations from idealised one-dimensional wave propagation. A simple method has been introduced to predict the heat of explosion for both $C_aH_bN_cO_d$ explosives, and explosives comprising mixtures or organic, inorganic and organometallic compounds. This method is useful to the first responder since an in-depth knowledge of the chemical or thermochemical properties of explosives is not required. Compared to TNT equivalence criteria published in literature, this procedure combines accuracy and simplicity to predict the performance of a wide range of energetic materials based on the valence of the atoms that exist within any composition, and at what stage reactions take place. The model also allows

the thermal energy release sequence to be predicted under ideal conditions should there be excess fuel in the composition and sufficient atmospheric oxygen to contribute to quaternary blast injuries.

Variance from reported literature does exist, but at a scale much reduced from other methods of TNT equivalence (no more than ±15% in examples as opposed to ±30%). This variance is a consequence of the unpredictable chemistry accompanying non-ideal detonations within the detonation and non-detonation reaction zones (for example the role of barium nitrate in Baratol and Baronal), or the enthalpies of formation that are chosen for complex hydrocarbons or polymers such as vaseline, diesel and sawdust. This paper demonstrates that the variance tends towards over-compensation, which from a risk and risk management perspective would be considered as low as reasonably practical.

As such, the valence equation can be used to determine the risk posed by HME as part of predictive performance analysis, therefore allowing evacuation distance for blast and fragmentation to be accurately determined. A general equation for approximate HME performance for a first responder can therefore be developed as a hand-held Application, providing timely levels of assurance whilst more complex interventions follow behind.

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Appendix A

Baseline calculations for FEFO – $C_5H_6N_4O_{10}F_{2(s)}$

$$\Omega = 15.999 \times \left(\frac{d - 2a - \frac{b}{2} + \frac{f}{2}}{molecular\ weight} \right) \times 100$$

$$\therefore \Omega = 15.999 \times \left(\frac{10 - 10 - \frac{6}{2} + 1}{320.12} \right) \times 100 = -9.99\%$$

$$\therefore products\ of\ detonation \rightarrow \frac{c}{2}N_2 + fHF + \left(\frac{b-f}{2}\right)H_2O + \left(2a - d + \frac{b-f}{2}\right)CO + \left(d - a - \frac{b-f}{2}\right)CO_2$$

$$\therefore C_5H_6N_4O_{10}F_2 \rightarrow \frac{4}{2}N_2 + 2HF + \left(\frac{6-2}{2}\right)H_2O + \left(10 - 10 + \frac{6-2}{2}\right)CO + \left(10 - 5 - \frac{6-2}{2}\right)CO_2$$

$$\therefore C_5H_6N_4O_{10}F_{2(s)} \rightarrow 2N_{2(g)} + 2HF_{(g)} + 2H_2O_{(g)} + 2CO_{(g)} + 3CO_{2(g)}$$

Baseline calculations for PBX 9407 – $C_{1.41}H_{2.66}N_{2.54}O_{2.69}Cl_{0.07}F_{0.09(s)}$

$$\Omega = 15.999 \times \left(\frac{d - 2a - \frac{b}{2} + \frac{f}{2} + \frac{cl}{2}}{molecular\ weight}\right) \times 100$$

$$\therefore \Omega = 15.999 \times \left(\frac{2.69 - 2(1.41) - \frac{2.66}{2} + \frac{0.09}{2} + \frac{0.07}{2}}{102.42}\right) \times 100$$

$$\therefore \Omega = 15.999 \times (-0.0135) \times 100 = -21.58\%$$

$$\therefore C_{1.41}H_{2.66}N_{2.54}O_{2.69}Cl_{0.07}F_{0.09} \rightarrow \frac{c}{2}N_2 + fHF + clHCl + \left(\frac{b-f-cl}{2}\right)H_2O + \left(2a - d + \frac{b-f-cl}{2}\right)CO + \left(d - a - \frac{b-f-cl}{2}\right)CO_2$$

$$\therefore C_{1.41}H_{2.66}N_{2.54}O_{2.69}Cl_{0.07}F_{0.09} \rightarrow \frac{2.54}{2}N_2 + 0.09HF + 0.07HCl + \left(\frac{2.66 - 0.09 - 0.07}{2}\right)H_2O + \left(2.82 - 2.69 + \frac{2.66 - 0.09 - 0.07}{2}\right)CO + \left(2.69 - 1.41 - \frac{2.66 - 0.09 - 0.07}{2}\right)CO_2$$

$$\therefore C_{1.41}H_{2.66}N_{2.54}O_{2.69}Cl_{0.07}F_{0.09(s)} \rightarrow 1.27N_{2(g)} + 0.09HF_{(g)} + 0.07HCl_{(g)} + 1.25H_2O_{(g)} + 1.38CO_{(g)} + 0.03CO_{2(g)}$$

Appendix B

Baseline calculations for ammonium nitrate/aluminium (88/12)

[Insert Table 11 here]

Note: Owing to the small molar proportions in 1g of explosive, up to six decimal places are used in calculations where required.

The aluminium competes with the detonation products formed, in this case $H_2O_{(g)}$ and any excess oxygen remaining upon formation of the detonation products. As this is a non-ideal explosive, the start point is Equation 19 to determine the oxygen balance for 1 g of composition:

$$\therefore \Omega = 15.999 \times \left(\frac{d - 2a - \frac{b}{2} - \frac{Li}{2} - \frac{Na}{2} - \frac{K}{2} + \frac{F}{2} + \frac{Cl}{2} + \frac{Br}{2} + \frac{I}{2} - Mg - Ba - Zn - Sr - \frac{3Al}{2} - \frac{3B}{2} - 2Pb}{1} \right) \times 100 \quad (19)$$

$$\therefore \Omega = 15.999 \times \left(\frac{d - 2a - \frac{b}{2} - \frac{3Al}{2}}{1} \right) \times 100$$

$$\therefore \Omega = 15.999 \times \left(\frac{0.032982 - \frac{0.043976}{2} - \frac{3}{2}(0.004447)}{1} \right) \times 100$$

$$\therefore \Omega = +6.92\%$$

The heat of explosion for this reaction is then determined from Hess' Law (see Equation 24), with enthalpy values taken from Table 4:

$$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f(products)} - \sum \Delta H^{\theta}_{f(reactants)} \quad (24)$$

$$\therefore H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447} \rightarrow \frac{c}{2}N_2 + \left(\frac{b}{2}\right)H_2O + aCO_2 + \left(\frac{2d - b}{4} - a\right)O_2 + alAl \; \{STAGE\ 1\}$$

$$\therefore H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447} \rightarrow \frac{0.021988}{2}N_2 + \left(\frac{0.043976}{2}\right)H_2O + \left(\frac{(2 \times 0.032982) - 0.043976}{4}\right)O_2 + 0.004447Al\ \{STAGE\ 1\}$$

$$\therefore H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447} \rightarrow 0.010994N_2 + 0.021988H_2O + 0.005497O_2 + 0.004447Al\ \{STAGE\ 1\}$$

$$\therefore Q_{Stage\ 1} = \{(0.021988\ \Delta\mathrm{Hf}(H_2O(g))\} - \{0.010994\ \Delta\mathrm{Hf}(AN(s))\}$$

$$\therefore Q_{Stage\ 1} = \{(0.021988 \times -241.8)\} - \{(0.010994 \times -365.3)\}$$

$$\therefore Q_{Stage\ 1} = -1.30\ kJg^{-1} = -1300\ kJkg^{-1}$$

At the end of Stage 1, the aluminium reacts with the product(s) of detonation as follows (see assumption 4 from Table 3):

$$0.021988H_2O + 0.005497O_2 + 0.004447Al \rightarrow 0.002224Al_2O_3 + 0.022027H_2O + 0.002160O_2\ \{STAGE\ 2\}$$

$$\therefore Q_{Stage\ 2} = \{(0.022027\Delta\mathrm{Hf}(H_2O(g)) + (0.002224 \times \Delta\mathrm{Hf}(Al_2O_3(s))\} - \{(0.021988 \times \Delta\mathrm{Hf}(H_2O(g))\}$$

$$\therefore Q_{Stage\ 2} = \{(0.022027 \times (-241.8)) + (0.002224 \times (-1669.8))\} - \{0.021988 \times (-241.8)\}$$

$$\therefore Q_{Stage\ 2} = \{-9.04\} - \{-5.32\} = -3720\ kJkg^{-1}$$

$$\therefore Q_{Stage\ 1} + Q_{Stage\ 2} = (-1300) + (-3720) = -5020\ kJkg^{-1}$$

Therefore, the calculated value of Q_e is 101.8% that of the reported literature value. Q_e in kJmo1^{-1} has been calculated as follows:

$$1\ mol\ NH_4NO_3 = 80.04\ g$$

$$1\ mol\ Al = 26.98\ g$$

$$\therefore 1000g\ mixture\ contains\ 880g\ NH_4NO_3 = 10.99\ mol$$

$$\therefore 1000g\ mixture\ contains\ 120g\ Al = 4.45\ mol$$

$$\therefore mol\%\ NH_4NO_3 = \left(\frac{10.99}{10.99 + 4.45}\right) \times 100 = 71.2\% = 56.97g$$

$$\therefore mol\%\ Al = \left(\frac{4.45}{10.99 + 4.45}\right) \times 100 = 28.8\% = 7.77g$$

$$\therefore 1\ mol = \ 64.77g$$

$$\therefore Q_{Stage\ 1} + Q_{Stage\ 2} = -5020 \times \left(\frac{64.77}{1000}\right) = -325.15\ kJmol^{-1}$$

$$\therefore H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447(s)} \rightarrow 0.010994N_{2(g)} + 0.022027H_2O_{(g)} + 0.00216O_{2(g)} + 0.002224Al_2O_{3(s)}$$

Appendix C

Baseline calculations for Baronal (barium nitrate/TNT/Al (50/35/15))

The equation for the above non-ideal explosive can be determined from Table 12 as follows:

$$C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556(s)}$$

[Insert Table 12 here]

The oxygen balance for Baronal is calculated using Equation 19:

$$\therefore \Omega = 15.999 \times \left(\frac{d - 2a - \frac{b}{2} - Ba - \frac{3}{2}Al}{1}\right) \times 100$$

$$\Omega = 15.999 \times \left(\frac{0.02072 - 2(0.01079) - \frac{1}{2}(0.0077) - 0.00191 - \frac{3}{2}(0.00556)}{1}\right) \times 100$$

$$\therefore \Omega = -23.92$$

Baronal is therefore oxygen deficient. The available oxygen cannot completely produce $CO_{2(g)}$ and $H_2O_{(g)}$. Therefore, the products of detonation can be determined from equation 11, remembering that *Ba* and *Al* shall react with the products of detonation in Stage 2:

$$\therefore products\ of\ detonation \rightarrow \frac{c}{2}N_2 + \left(\frac{b}{2}\right)H_2O + \left(a - \left(d - a - \frac{b}{2}\right)\right)CO + \left(d - a - \frac{b}{2}\right)CO_2$$

Therefore, $Q = \sum \Delta H^{\theta}_{f(products)} - \sum \Delta H^{\theta}_{f(reactants)}$ *(21)*

$$\therefore C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556} \rightarrow \frac{0.00845}{2}N_2 + \frac{0.0077}{2}H_2O + \left(0.01079 - \left(0.02072 - 0.01079 - \frac{0.0077}{2}\right)\right)CO + \left(0.02072 - 0.01079 - \frac{0.0077}{2}\right)CO_2$$

$$\therefore C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556} \rightarrow 0.004225N_2 + 0.00385H_2O + 0.00471CO + 0.00608CO_2 + 0.00191Ba + 0.00556Al\ \{STAGE\ 1\}$$

$$\therefore Q_{Stage\ 1} = \{(0.00385\ \Delta\mathrm{Hf}(H_2O)) + (0.00471\Delta\mathrm{Hf}(CO)) + (0.00608\Delta\mathrm{Hf}(CO_2))\} - \{(0.001541 \times \Delta\mathrm{Hf}(\mathrm{TNT})) + (0.001913\Delta\mathrm{Hf}(\mathrm{Ba}(NO_3)_2) + (0.005559\Delta\mathrm{Hf}(\mathrm{Al}))\}$$

$$\therefore Q_{Stage\ 1} = \{(0.00385 \times (-241.8)) + (0.00471 \times (-110.5)) + (0.00608 \times (-393.5))\} - \{(0.001541 \times (-62.07)) + (0.001913 \times (-998)) + (0.005559 \times 0)\}$$

$$\therefore Q_{Stage\ 1} = \{-0.931 - 0.520 - 2.392\} - \{-0.0956 - 1.91\} = -1.837kJ/g$$

$$\therefore Q_{Stage\ 1} = -1837kJkg^{-1}$$

$$\therefore 0.0042N_2 + 0.00385H_2O + 0.00471CO + 0.00608CO_2 + 0.00191Ba + 0.00556Al \rightarrow 0.0042N_2 + 0.00385H_2O + 0.00471CO + 0.000955CO_2 + 0.005125C + 0.00191BaO + 0.00278Al_2O_3\ \{STAGE\ 2\}$$

$$\therefore Q_{Stage\ 2} = \{(0.00385\Delta\mathrm{Hf}(H_2\mathrm{O}) + (0.00471\Delta\mathrm{Hf}(CO)) + (0.000955\Delta\mathrm{Hf}(CO_2)) + (0.00191\Delta\mathrm{Hf}(\mathrm{BaO})) + (0.00278\Delta\mathrm{Hf}(Al_2O_3))\} - \{(0.00385\Delta\mathrm{Hf}(H_2\mathrm{O})) + (0.00471\Delta\mathrm{Hf}(CO)) + (0.00608\Delta\mathrm{Hf}(CO_2))\}$$

However, the ΔH_f for H_2O and CO cancel out, as their quantities have not been altered:

$$\therefore Q_{Stage\ 2} = \{(0.000955\Delta\mathrm{Hf}(CO_2)) + (0.00191\Delta\mathrm{Hf}(\mathrm{BaO})) + (0.00278\Delta\mathrm{Hf}(Al_2O_3))\} - \{(0.00608\Delta\mathrm{Hf}(CO_2))\}$$

$$\therefore Q_{Stage\ 2} = \{(0.000955 \times (-393.5)) + (0.00191 \times (-548.1)) + (0.00278 \times (-1669.8))\} - \{(0.00608 \times (-393.5))\}$$

$$\therefore Q_{Stage\ 2} = \{(-0.376) + (-1.047) + (-4.642\} - \{(-2.39)\}$$

$$\therefore Q_{Stage\ 2} = \{(-6.065) - (-2.39)\} = -3.675$$

$$\therefore Q_{Stage\ 2} = -3675 kJkg^{-1}$$

$$\therefore Q_{Stage\ 1} + Q_{Stage\ 2} = (-1837) + (-3675) = -5512 kJkg^{-1}$$

$$\therefore TNT_e = \frac{-5512}{-4091} = 1.34$$

Therefore, the calculated value of Q_e is 114% that of the reported literature value. Q in kJmol^{-1} can be calculated as follows:

$$1mol\ Ba(NO_3)_2 = 261.337g$$

$$1mol\ TNT = 227.13g$$

$$1\ mol\ Al = 26.98g$$

$$\therefore 1000g\ mixture\ contains\ 500g\ Ba(NO_3)_2 = 1.91mol$$

$$\therefore 1000g\ mixture\ contains\ 350g\ TNT = 1.54mol$$

$$\therefore 1000g\ mixture\ contains\ 150g\ Al = 5.55mol$$

$$\therefore mol\%\ Ba(NO_3)_2 = \left(\frac{1.91}{1.91 + 1.54 + 5.55}\right) \times 100 = 21.2\% = 55.4g$$

$$\therefore mol\%TNT = \left(\frac{1.54}{1.91 + 1.54 + 5.55}\right) \times 100 = 17.1\% = 38.84g$$

$$\therefore mol\%Al = \left(\frac{5.55}{1.91 + 1.54 + 5.55}\right) \times 100 = 61.7\% = 16.64g$$

$$\therefore 1\ mol = 110.88g$$

$$\therefore Q_{Stage\ 1} + Q_{Stage\ 2} = -5512 \times \left(\frac{110.88}{1000}\right) = -611.17 kJmol^{-1}$$

$$\therefore C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556(s)} \rightarrow 0.004225N_{2(g)} + 0.005125C_{(s)} + 0.00385H_2O_{(g)} + 0.00471CO_{(g)} + 0.000955CO_{2(g)} + 0.00191BaO_{(s)} + 0.00278Al_2O_{3(s)}$$

Tables and Figures

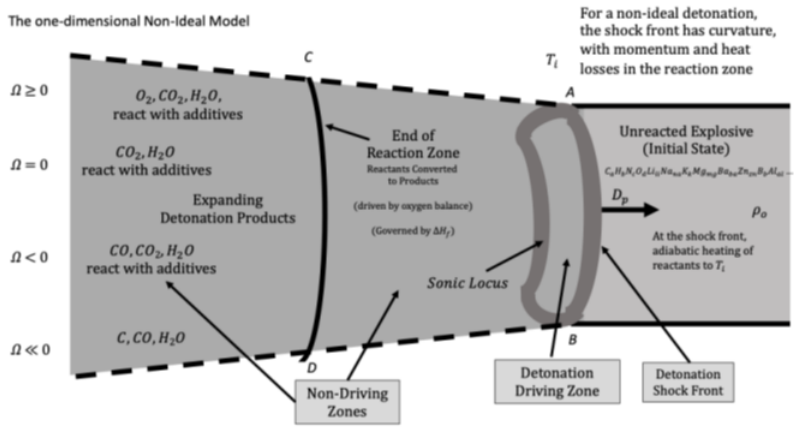

Table 1 Energy release sequence in an explosive energised by aluminium

Stage	Event	Timescale
1	Anoxic Detonation – heat is produced from the *'detonation driving zone'* as the shock front dissociates explosive molecules. No apparent temperature rise from ignition temperature (T_i) is observed until the detonation products form.[23, 25, 39, 40] The heat of explosion *(Q_e)* can be calculated based on the molecular composition of the non-ideal explosive and Hess' law,[38] regardless of the physical charge structure. The explosion products e.g. $CO_{(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ are first produced from the active radical species, based on thermochemistry and oxygen balance. Additives do not participate in this highly exothermic reaction zone and act as an inert material, even absorbing and consuming part of the heat liberated, thereby reducing the total energy of the detonation wave. A drop in the detonation pressure (D_{cj}/D_p) denotes this.	The induction zone can take as little as 0.1 ns to dissociate the explosive into radical species. The reaction zone for ideal explosives such as HMX and TNT ranges from 20 – 80 ns.
2	Anaerobic Combustion – the explosion products produced in Stage 1 then react with additives under the high temperature and pressure environment behind the	10's to 100's of µs.

	C-J plane. Dependent upon the combustion products, the heat of explosion increases at the expense of gas volume. For metal explosives, the major products that liberate heat other than water, carbon monoxide and carbon dioxide can be metal carbonate, metal hydride, metal hydroxide, metal nitrate, metal nitride, and metal oxide. [25, 37, 41]	
3	Aerobic Combustion – if any additives remain within the non-ideal explosive after anaerobic combustion finishes, reactions then take place with oxygen in the atmosphere. It is assumed that full combustion takes place with atmospheric oxygen over a period of ms, and that this thermal energy release does not contribute to mechanical work, but rather the additional heat energy available to interact with the environment. [37, 42 - 45]	10's of ms

Table 2 Outline method

STEP	Description
1. The establishment of a baseline programme in excel	As this is a proof of concept, an excel spreadsheet is constructed to determine oxygen balance (Ω) and heat of explosion for ideal compositions comprising empirical formula *CHNO*. The molar proportions of each atom in one gram of explosive are established to determine Q_e from Hess' Law. Kistiakowsky-Wilson and modified Kistiakowsky-Wilson rules are used as the primary vehicle to develop the likely products of detonation based upon the proportion(s) of fuel(s) and oxidiser(s) and detonation theory. The spreadsheet values are then interrogated against known literature values of Q_v for those ideal explosives to determine baseline accuracy of Q_e and Ω calculations. Comparison of Q_e/Q_v should be unity.
2. Derivation of formula for non-ideal explosives	A formula is then devised for the heat of explosion for non-ideal compositions, which could take any form from Equation 1. This formula is then tested against the molecular formulae for the ideal *CHNO* explosive compositions examined in Step 1 to ensure that the values of Q_e and Ω obtained are identical. If this is not the case, then the formula in Step 2 is fundamentally flawed. Assumptions are clearly articulated to facilitate understanding and to influence refinement/automation of future models.
3. The introduction of powdered metals	Since so much literature is available on aluminium as an additive, aluminium is then introduced to the revised non-ideal explosive formula for TNT and ammonium nitrate (AN) compositions. This is to gain confidence in the thermochemical calculations. The oxygen balance and heat of explosion are then calculated and compared against open-source literature values using the energy release sequence in Table 1. Results of Q_e are compared to Q_v values reported in literature. Values of TNT_e are then calculated using Equation 2.
4. The introduction of	Non-ideal explosives of varied molecular composition are then interrogated with Q_e/Ω compared to open-source literature values. This step determines that the calculator can manipulate

varied fuel and oxidiser mixtures	explosive compositions containing multiple fuels and oxidisers with confidence.

Table 3: Assumptions

Assumption	Description
1.	Atoms want to achieve their highest oxidation state, which is also their lowest internal energy state. This means that the products of detonation of $C_aH_bN_cO_d$ explosives will strive to form $CO_{2(g)}$ and $H_2O_{(g)}$, dependent upon available oxygen (Kistiakowsky-Wilson and modified Kistiakowsky-Wilson rules apply).
2.	Additives do not react with $CO_{(g)}$, $CO_{2(g)}$ or $H_2O_{(g)}$ until those products of detonation have been formed from the active radicals.
3.	That there is sufficient hydrogen in the non-ideal explosive to bind *Cl, Br, I* and *F* to *HF, HCl, HI, HBr* etc
4.	The model assumes that more reactive elements of the non-ideal explosive compound form detonation products based on the hierarchy of the heats of reaction.[25] Additive oxidation will therefore commence with those detonation products with the highest enthalpies of formation. For example, $Al_{(s)}$ will compete with $CO_{2(g)}$ before it will progress to $H_2O_{(g)}$ and $CO_{(g)}$ to form $Al_2O_{3(s)}$. And, although $S_{(s)}$ and $Hg_{(l)}$ can have differing valence (*S*=2,4 and 6, *Hg* = 1, 2) the most favourable energy states such as $SO_{2(g)}$ (ΔH_f -296.1 kJmol^{-1}) and $HgO_{(s)}$ (ΔH_f -90.7 kJmol^{-1}) would be considered by the calculator.

Table 4 Enthalpies of formation used in calculations

Species	Phase	Empirical Formula	Enthalpy of Formation $\triangle H_f$ (kJmol^{-1})
Aluminium	Solid	Al	0.0
Aluminium Oxide	Solid	Al_2O_3	-1669.8
Ammonium Nitrate	Solid	NH_4NO_3	-365.3
Barium	Solid	Ba	0.0
Barium Nitrate	Solid	$Ba(NO_3)_2$	-988.0
Barium Oxide	Solid	BaO	−558.1
Baratol	Solid	$C_{0.028}H_{0.02}N_{0.013}O_{0.026}Ba_{0.00038}$	-295.0
Carbon	Solid	C	0.0
Carbon Dioxide	Gas	CO_2	-393.5
Carbon Monoxide	Gas	CO	-110.5
Diesel	Liquid	$C_{12}H_{23}$	-355.9
Hydrogen	Gas	H_2	0.0
Hydrogen Chloride	Gas	HCl	-92.3
Hydrogen Fluoride	Gas	HF	-268.6

Hydrogen Peroxide	Liquid	H_2O_2	-187.6
Lead Azide	Solid	$Pb(N_2)_3$	468.6
Nitrogen	Gas	N_2	0.0
Nitroglycerine	Liquid	$C_3H_5N_3O_9$	-370.7
Paraffin Wax	Liquid	$C_{25}H_{52}$	-2460.5
PETN	Solid	$C_5H_8N_4O_{12}$	-530.5
RDX	Solid	$C_3H_6N_6O_6$	+70.3
TATP	Solid	$C_9H_{18}O_6$	-151.18
TNT	Solid	$C_7H_5N_3O_6$	-62.1
3-NT	Liquid	$C_7H_7NO_2$	-31.5
Water	Gas	H_2O	-241.8
Wood Meal	Solid	$C_{50}H_{72}O_{33}$	-945.8

Notes for Table 4: Enthalpies of formation used for calculations in this paper are taken from literature.[21, 27, 56, 58-63] Equations refer to the phase of each compound (solid, liquid or gas). For example, where H2O is quoted, this means H2O(g), not H2O(s) or H2O(l).

[5]

Table 5 Group and valence entry points

Group Valence	Remarks
1 and 7 (Valence ±1)	*K, Na, F* and *Cl* are highly reactive and possess valance +1/-1 respectively. This is therefore the entry point for atoms with valance +1/-1
2 and 6 (Valence ±2)	*Ca, Mg* and *O* are valances +2/-2 respectively. This is therefore the entry point for atoms with valance +2/-2
3 (Valence ±3)	*Al* and *B* require 3/2 oxygen (valance 3). This is therefore the entry point for metals with valence +3/-3
4 (Valence ±4)	*C* requires two oxygen atoms to achieve their preferred energy state (valence 4). This is therefore the entry point for HME compositions containing atoms with valance +4/-4

Table 6 Literature and formula values for Q and oxygen balance for ideal and non-ideal explosives

Explosive	Literature Values			Formula Values		
	Q_v (kJmol^{-1})	Ω	*Reference*	Q_e (kJmol^{-1})	Ω	$\left(\frac{Q_e}{Q_v} \times 100\%\right)$
TNT	-929.34 (-4091.63)[1]	-73.90	[27]	-929.30	-73.90	100.00
RDX	-1127.36 (-5075.50)	-21.60	[27]	-1118.90	-21.60	99.25
RDX/TNT (60/40)	-1057 (-4684)	-42.60	[27]	-1057	-42.60	100.00
NG	-1414.40 (-6228.46)	+3.50	[27]	-1414	+3.50	99.99
TNT/Al (80/20)	-756.36 (-5275)	-67.60	[10]	-786.60	-67.60	104.00
AN/Al (88/12)	-319.50 (-4934)	+6.92	[55]	-325.15	+6.90	101.80

Table 7 Reaction sequence for AN/Al (88/12)

Process	Products of Detonation	Q_e (kJkg^{-1})	Q_e (kJmol^{-1})
Stage 1	$H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447} \rightarrow 0.010994\ N_2 + 0.021988\ H_2O + 0.005497\ O_2 + 0.004447\ Al$	-1300	

[1] Figures in (parenthesis) denote literature values for Q_v in kJkg^{-1}.

Stage 2	$0.021988H_2O + 0.005497\ O_2 + 0.004447\ Al \rightarrow 0.002224\ Al_2O_3 + 0.022027\ H_2O + 0.002160\ O_2$	-3720	
Totals	$H_{0.043976}N_{0.021988}O_{0.032982}Al_{0.004447(s)} \rightarrow 0.010994\ N_{2(g)} + 0.022027\ H_2O_{(g)} + 0.00216\ O_{2(g)} + 0.002224\ Al_2O_{3(s)}$	-5020	-325.15
$\left(\frac{Q_e}{Q_v}\right) \times 100\% = \frac{5020}{4934} \times 100\% = 101.8\%$			
$\left(\frac{Q_e}{Q_{tnt}}\right) \times 100\% = \frac{5020}{4091} \times 100\% = 122.7\%$			

Table 8 Reaction sequence for Baronal

Process	Products of Detonation	Q_e (kJkg^{-1})	Q_e (kJmol^{-1})
Stage 1	$C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556} \rightarrow 0.004225\ N_2 + 0.00385\ H_2O + 0.00471\ CO + 0.00608\ CO_2 + 0.00191\ Ba + 0.00556\ Al$	-1837	
Stage 2	$0.0042\ N_2 + 0.00385\ H_2O + 0.00471\ CO + 0.00608\ CO_2 + 0.00191\ Ba + 0.00556\ Al \rightarrow 0.0042\ N_2 + 0.00385\ H_2O + 0.00471\ CO + 0.000955\ CO_2 + 0.005125\ C + 0.00191\ BaO + 0.00278\ Al_2O_3$	-3675	
Totals	$C_{0.01079}H_{0.0077}N_{0.00845}O_{0.02072}Ba_{0.00191}Al_{0.00556(s)} \rightarrow 0.004225\ N_{2(g)} + 0.005125\ C_{(s)} + 0.00385\ H_2O_{(g)} + 0.00471\ CO_{(g)} + 0.000955\ CO_{2(g)} + 0.00191\ BaO_{(s)} + 0.00278\ Al_2O_{3(s)}$	-5512	-611.17

$\left(\frac{Q_e}{Q_v}\right)$	$\left(\frac{5512}{4767}\right) \times 100\%$	114%
$\left(\frac{Q_e}{Q_{tnt}}\right)$	$\left(\frac{5512}{4091}\right) \times 100\%$	135%

Note for Table 8: These values demonstrate an identical prediction of oxygen balance and Q_e within 14% of Q_v for baronal[54, 66] (-4767 kJkg^{-1}).

[5]

Table 9 Comparison of non-ideal explosive heats of explosion to literature

Explosive	Literature		Products of Detonation (to 5.S.F.)	Ω	Q_e (kJkg^{-1})	$\left(\frac{Q_e}{Q_v}\right)$
	(Q_v)	Ref.				
ANFO (96/4) (Diesel $C_{12}H_{23}$)	-3950	67	$C_{0.00287}H_{0.05347}N_{0.02399}O_{0.03598}$ $\rightarrow 0.01199\ N_{2(g)}$ $+ 0.02674\ H_2O_{(g)}$ $+ 0.00287\ CO_{2(g)}$ $+ 0.00175\ O_{2(g)}$	+5.61	-4438.5	1.12 (112%)
AN/Al (60/40)	-8866	24	$H_{0.02998}N_{0.01499}O_{0.02249}Al_{0.01483(s)}$ $\rightarrow 0.00750\ N_{2(g)}$ $+ 0.00025\ H_2O_{(g)}$ $+ 0.01474\ H_{2(g)}$ $+ 0.00741\ Al_2O_{3(s)}$	-23.6	-9683.1	1.09 (109%)

ANFO/Al (92/5/3)	-4328	68	$C_{0.00359}H_{0.05285}N_{0.02299}O_{0.03448}Al_{0.00111(s)} \rightarrow 0.01149\ N_{2(g)} + 0.00039\ C_{(s)} + 0.02642\ H_2O_{(g)} + 0.00320\ CO_{2(g)} + 0.00056\ Al_2O_{3(s)}$	-1.25	-4304.8	0.99 (99%)
Barium Nitrate/TNT (10/90) – Baratol	-4029	69	$C_{0.02774}H_{0.01981}N_{0.01265}O_{0.02607}Ba_{0.00038(s)} \rightarrow 0.00633\ N_{2(g)} + 0.01636\ C_{(s)} + 0.00991\ H_2O_{(g)} + 0.00698\ CO_{(g)} + 0.00440\ CO_{2(g)} + 0.00038\ BaO_{(s)}$	-63.50	-4652.7	1.15 (115%)
AN/TNT/NG (70/25/5) Donarite	-3559	61	$C_{0.00555}H_{0.04438}N_{0.02263}O_{0.03573(s)} \rightarrow 0.01132\ N_{2(g)} + 0.02219\ H_2O_{(g)} + 0.00555\ CO_{2(g)} + 0.00122\ O_{2(g)}$	+3.91	-3773.4	1.06 (106%)
AN/TNT/AL (40/40/20) – Minol 2	-6782	66	$C_{0.01233}H_{0.02880}N_{0.01528}O_{0.02556}Al_{0.00741(s)} \rightarrow 0.00764\ N_{2(g)} + 0.00117\ C_{(s)} + 0.00330\ H_2O_{(g)} + 0.01116\ CO_{(g)} + 0.00371\ Al_2O_{3(s)} + 0.01112\ H_{2(g)}$	-39.38	-6900.1	1.02 (102%)

$KClO_3$/Vaseline (90/10) - Cheddite	-4961	69	$C_{0.00572}H_{0.01190}O_{0.02203}K_{0.00734}Cl_{0.00734(s)} \rightarrow 0.00155\ KClO_{3(s)} + 0.00595\ H_2O_{(g)} + 0.00572\ CO_{2(g)} + 0.00580\ KCl_{(s)}$	+7.42	-5913.9	1.19 (119%)
Lead Azide (PbN_6)	-1610	27, 63	$Pb_{0.00172}N_{0.0206(s)} \rightarrow 0.00172\ Pb_{(s)} + 0.01030\ N_{2(g)}$	-5.49	-1609.0	1.00 (100%)

Table 10 Performance of non-ideal compositions without literature reference

Explosive	**Products of Detonation (to 5.S.F.)**	$\boldsymbol{\Omega}$	$\boldsymbol{Q_e}$ **(kJkg^{-1})**	$\left(\frac{\boldsymbol{Q_e}}{\boldsymbol{Q_{TNT}}}\right)$
H_2O_2/Sawdust (80/20) Concentrated Hydrogen Peroxide (CHP)	$C_{0.00833}H_{0.05903}O_{0.05253} \rightarrow 0.02951\ H_2O_{(g)} + 0.00833\ CO_{2(g)} + 0.00318\ O_{2(g)}$	+10.19	-5842.9	1.43
Sodium Chlorate/Nitroben zene (72/28) (CO-OP Explosive)	$C_{0.01365}H_{0.01137}N_{0.00227}O_{0.02484}Na_{0.00676}Cl_{0.00676(s)} \rightarrow 0.00114\ N_{2(g)} + 0.00814\ CO_{(s)} + 0.00569\ H_2O_{(g)} + 0.00551\ CO_{2(g)} + 0.00676\ NaCl_{(s)}$	-13.01	-4904.1	1.12
AN/TATP/Al (85/5/10)	$C_{0.00203}H_{0.04653}N_{0.02124}O_{0.03321}Al_{0.00371(s)} \rightarrow 0.01062\ N_{2(g)} + 0.02326\ H_2O_{(g)} + 0.00185\ Al_2O_{3(s)} + 0.00203\ CO_{2(g)}$	+0.54	-4057.0	1.00

Table *11*: Molecular formula calculation for AN-Al (88/12)

Molecule	Empirical Formula	Proportion by Mass (g)	Molecular Weight (g)	Molar Proportions in 1g	C	H	N	O	Al
Ammonium Nitrate	NH_4NO_3	0.88	80.043480	0.010994	0	4	2	3	0
Aluminium	Al	0.12	26.981540	0.004447	0	0	0	0	1
TOTALS		1		0.015442	0	0.043976	0.021988	0.032982	0.004447

5

Table 12: Non-ideal formula for Baronal (90/10)

Molecule	Empirical Formula	Proportion by Mass (g)	Molecular Weight (g)	Molar Proportions in 1g	C	H	N	O	Ba	Al
TNT	$C_7H_5N_3O_6$	0.35	227.13	0.001541	7	5	3	6	0	0

Al	Al	0.15	26.98	0.005559	0	0	0	0	0	1
Barium Nitrate	$Ba(NO_3)_2$	0.5	261.34	0.001913	0	0	2	6	1	0
TOTALS		1		0.009014	0.01079	0.0077	0.00845	0.02072	0.00191	0.00556

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Calculating the heat of explosion for non-ideal explosives

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