

Chemical Principles Governing Energy Release in Munition Design: Thermodynamics,
Thermochemistry, and Application to an 81 mm Mortar.

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10/01/2026

I. Abstract

Chemical principles were evaluated as the governing framework for energetic material performance across the munition lifecycle, with emphasis placed on the design stage and the mechanisms of energy release. A conventional 81 mm mortar bomb was used as the reference system to anchor how chemical behaviour maps to fuze initiation, main fill detonation, propellant deflagration, and casing break-up. The First Law was used to frame the fixed energy budget for an event through $\Delta U = Q - W$, and to justify the use of TNT equivalence and warhead energy partitioning approaches for estimating the balance between casing work and blast output. The Second Law was used to explain irreversibility and efficiency limits through entropy increase during conversion of an ordered solid into hot gases and fragments. Composition-driven effects were treated using CHNO thermochemistry, oxygen balance as a predictor of product set and temperature potential, and heats of formation to estimate heat of explosion Q in $\text{kJ} \cdot \text{kg}^{-1}$. Product-gas behaviour was linked to equations of state and hydrocode modelling as the route from chemical energy release to pressure histories, casing fracture, and fragment velocity. The overall conclusion was that chemical principles set the achievable performance envelope, while real munition behaviour is shaped by platform constraints, variability, ageing, safety requirements, and end-of-life considerations

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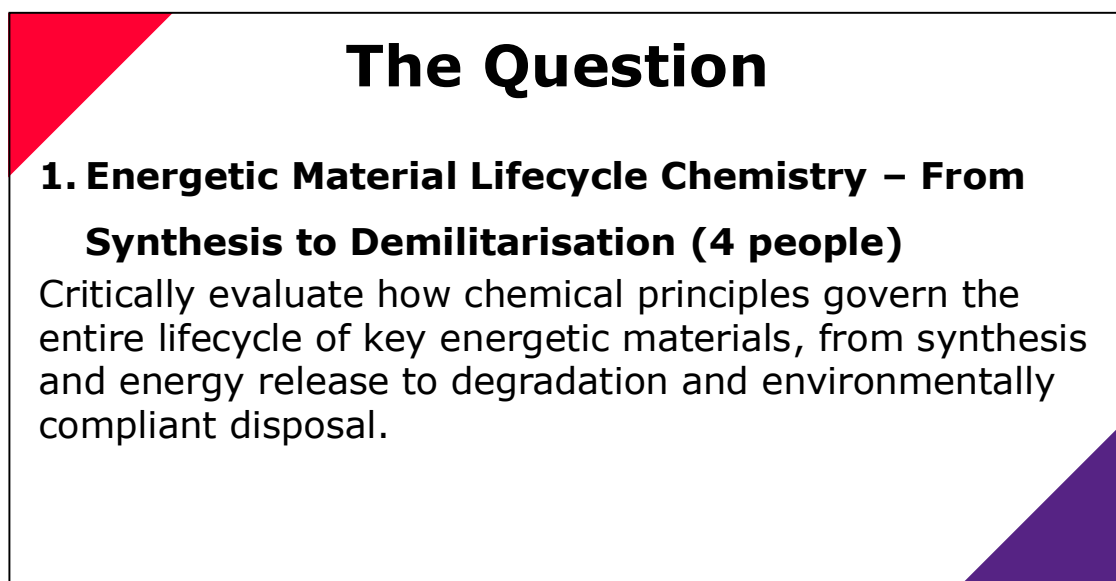
1. Individual Technical Summary Group Specification

The group brief was to:

“Critically evaluate how chemical principles govern the entire lifecycle of key energetic materials, from synthesis and energy release to degradation and environmentally compliant disposal.”

On the introductory figures (Figures 1, 2), the lifecycle was divided into design, manufacture, in service behaviour, and disposal. This contribution covered the design stage, focusing on the question:

“How do chemical principles that govern energy release constrain and enable munition design?”



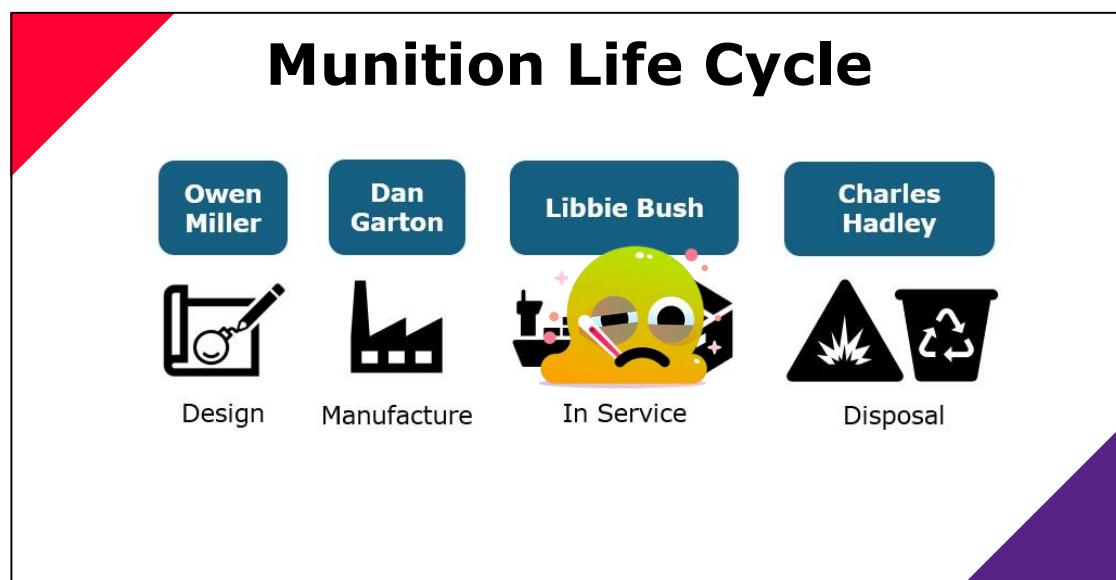
The Question

1. Energetic Material Lifecycle Chemistry – From Synthesis to Demilitarisation (4 people)

Critically evaluate how chemical principles govern the entire lifecycle of key energetic materials, from synthesis and energy release to degradation and environmentally compliant disposal.

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Figure 1 – The Group Question

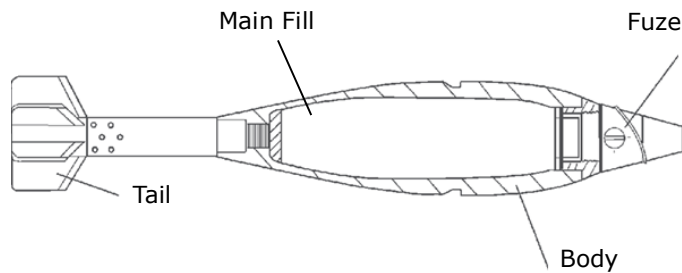


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Figure 2 – Munition Life Cycle

A conventional 81 mm mortar bomb was used as a reference system (Figure 3). Its body, fuze, tail, and main fill illustrated how the chemistry of energetic materials is linked to component level design, although the system is referred to more generally as “the munition” in this summary.

The Munition: 81mm Mortar



A typical 81mm Mortar will be used as the example throughout this lifecycle presentation.

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Figure 3 – The Munition: 81mm Mortar [1] [2]

2. Thermodynamic framing

Energetic behaviour was first linked to the laws of thermodynamics (Figure 4). During burning, deflagration, or detonation, chemical bond energy is converted into heat, high pressure gas, and mechanical work on the surroundings. In the munition, this work appears as blast loading and case fragmentation. The First and Second Laws provide the basic rules for these transformations and must be satisfied in any realistic design [3].

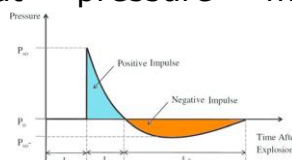
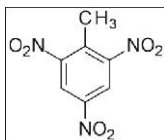
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Laws of Thermodynamics in Energetics

Laws of thermodynamics describe how energy behaves in physical systems.



chemical energy $\rightarrow$ heat $\rightarrow$ pressure $\rightarrow$ mechanical work.



Understanding these laws is essential for:

Predicting energy transformations during rapid decomposition of explosive materials.

Designing munitions that deliver controlled, repeatable energy release.

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Ref: [1], [2]

Figure 4 – Laws of Thermodynamics in Energetics

The First Law was then applied using the example in Figure 5. The internal energy of the system is the heat released by reaction minus the mechanical work performed.

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First Law, Work & Heat in Explosives

First Law of thermodynamics:
energy cannot be created or destroyed, only transferred or converted from one form to another

$\Delta U = Q - W$ – change in internal energy of the explosive + products

Q – heat supplied to the system

W – mechanical work done by the system on its surroundings

In an explosive event, chemical bond energy is converted into internal energy; expanding gases then perform mechanical work on the case and the air.

For gas expansion against external pressure: a large increase in volume at high pressure gives a large amount of work available for blast and fragmentation.

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Example: 81mm Mortar TNT, energy left once case has fragmented

$$W_b = 1.19 \left[\frac{1 + Mr(1 - Mc)}{1 + Mr} \right] C$$

$$Mr = \text{Mass Ratio} = \frac{\text{Case mass}}{\text{Charge Mass}}$$

$C = \text{Mass of Charge}$

$Mc = \text{whole confinement}$

$$Mr = 2 = 1.8/0.9$$

$$C = 0.9$$

$$Mc = 1$$

$$W_b = 1.19 \left[\frac{1 + 2(1 - 1)}{1 + 2} \right] 0.9$$

$$W_b = 0.357 \text{ Barecharge TNTe}$$

Ref: [1], [3]

Figure 5 – First Law, Work & Heat in Explosives

For an explosive this means that the reaction enthalpy is divided between the internal energy of the products and the $P\Delta V$ work that breaks and accelerates the case and drives the blast wave. This is the basis for TNT equivalence. For a 0.9 kg TNT filled munition, the available chemical energy is 0.9 kg TNT equivalent. Empirical relationships from [4] Warheads were used to show how part of this energy is consumed in case fragmentation and how the remaining TNT equivalent is then used in blast calculations [3].

The key point is that design does not change the total energy, it only changes how a fixed amount of chemical energy is split between different effects.

3. Reaction mode: deflagration versus detonation

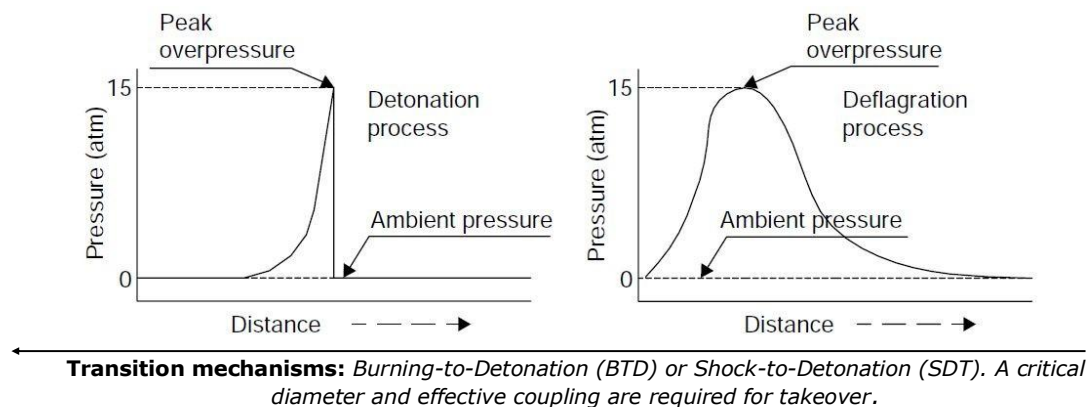
The mode of energy release was then considered (Figure 6). Deflagration was described as a subsonic surface reaction controlled mainly by heat and mass transfer, often with atmospheric oxygen involved in the case of tail propellants. Detonation was defined as a supersonic shock supported reaction front moving through the energetic mass, with reaction occurring in the high-pressure products behind the shock [5].

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Detonation vs Deflagration

Detonation: *Supersonic, shock-supported reaction front; energy transfer via compression waves; near-constant VoD for a given explosive and density.*

Deflagration: *Subsonic surface reaction; heat/pressure diffusion governs rate. Confinement increases burn speed but no internal shock.*



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Ref: [4], [5]

Figure 6 – Detonation vs Deflagration

Whether a given formulation and geometry will detonate or only burn depends on reaction kinetics, critical density, critical diameter, crystal microstructure, and confinement [6]. Burning to detonation transition occurs when a confined deflagration accelerates until a self-sustaining detonation forms. This behaviour is required in the fuze train where a small initiating stimulus must reliably drive the booster and main fill, but it is unacceptable in the propellant bed where only controlled deflagration is required. Fill

selection and charge layout must therefore ensure that detonation occurs only in the intended parts of the munition [7].

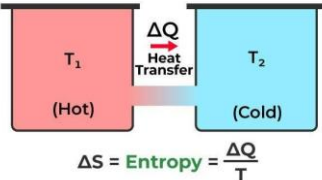
4. Second Law, entropy, and efficiency

The Second Law was linked to explosive performance through entropy, with an illustrative hot to cold system shown in Figure 7 [3]. Entropy was described as a measure of how widely energy is spread within a system. Heat flows from hot to cold increasing total entropy; the reverse process does not occur without external work.

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Second Law, Entropy & Explosive Efficiency

the total entropy, or disorder, of a closed system can only increase over time



- Heat flows naturally from the hot block to the cold block.
- As this happens, energy that was concentrated in the hot block becomes more spread out between both blocks.
- That spreading-out of energy is what is called an increase in entropy.
- The process doesn't reverse by itself as you never see heat flow from cold to hot without doing work, which is the essence of the Second Law.

In Energetics:

- Detonation turns an ordered solid into hot gases and moving fragments, so the energy becomes much more spread out and the entropy increases.
- Some of that energy appears as organised motion (blast, fragment velocity); the rest goes into heating gases, air and fragments in a highly irreversible way.
- In design we care how much of the total chemical energy feeds the desired damage mechanisms, within the limits set by this unavoidable spreading-out of energy.

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Ref: [1], [6]

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Figure 7 – Second Law, Entropy & Explosive Efficiency

In a detonating munition, an ordered crystalline solid is converted into hot gases and moving fragments [7]. Energy is spread over many degrees of freedom and entropy increases. Only part of the reaction enthalpy appears as organised motion, such as

fragment kinetic energy and blast impulse. The rest appears as random thermal motion and irreversible heating of products, air, and casing [5], this affects design. If natural fragmentation alone is relied on, variations in material flaws and local stresses can cause large shot to shot differences. The use of preformed fragments was highlighted to control how energy is channelled into fragments, while accepting that the overall increase in entropy cannot be avoided.

5. Oxygen Balance & Thermochemistry

The link from molecular structure to products and energy density was made through oxygen balance and thermochemistry (Figures 8 and 9). Oxygen balance shows whether a CHNO explosive has enough oxygen to convert all carbon to carbon dioxide and all hydrogen to water [8]. TNT has a strongly negative oxygen balance and is oxygen deficient, its idealised products include carbon monoxide and solid carbon as well as carbon dioxide, water, and nitrogen. Fuel rich compositions tend to be more stable and easier to process but have lower flame temperature and lower specific energy. Compositions with near zero or slightly positive oxygen balance give hotter gases, higher detonation pressures, and greater specific energy, but usually higher sensitivity and more demanding insensitive munitions performance [3].

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Oxygen Balance & Product Composition

Oxygen balance (OB) indicates whether there is enough oxygen in the molecule to fully oxidise C and H to CO₂ and H₂O:

$$\Omega = \frac{d - 2a - \frac{b}{2}}{MW} \times 1600$$

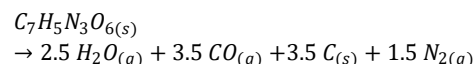
TNT has a strongly negative OB → oxygen-deficient (-74%). products include CO and solid carbon.

Design consequences:

- Fuel-rich explosives: slightly lower flame temperature, more soot and CO, often reduced sensitivity and good casting behaviour.
- Near-zero or slightly positive OB formulations: hotter, cleaner gases and higher performance, but usually more sensitive.

Example: TNT

Products of TNT – C₇H₅N₃O₆



$$\Omega = \frac{d - 2a - \frac{b}{2}}{MW} \times 1600$$

$$\therefore \Omega = \frac{6 - 14 - \frac{5}{2}}{227} \times 1600 = -74\%$$

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Ref: [2], [7]

Figure 8 – Oxygen Balance & product Composition

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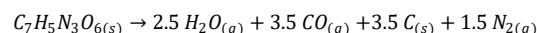
Thermochemistry of CHNO Explosives

- Thermochemistry turns the OB formula into a numerical energy per kg, using heats of formation and product rules.
- That specific energy is the chemical fuel for the detonation: it sets the upper limit on product temperature, pressure and PΔV work.
- Comparing Q (kJ·kg⁻¹) between explosives allows the rank of fills by energy density and see what extra performance we gain over TNT.
- The same thermochemical data feed into EOS and hydrocode models, so this is the link from molecular structure → predicted blast and fragmentation.

Table 5.5 Modified Kistiakowsky–Wilson rules

Rule no.	Conditions
1	Hydrogen atoms are converted to water
2	If any oxygen remains then carbon is converted to carbon monoxide
3	If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4	All the nitrogen is converted to nitrogen gas, N ₂

Product Energy Outputs	
Compound	ΔH _f (kJ/mol)
TNT _(s)	-26.10
RDX _(s)	+62.00
C _(s)	00.00
CO _{2(g)}	-393.50
CO _(g)	-110.50
H ₂ O _(g)	-241.80
N _{2(g)}	00.00
O _{2(g)}	00.00



$$\therefore Q = [(\Delta H_f \text{ Products}) - (\Delta H_f \text{ Reactants})]$$

$$\therefore Q = [(\Delta H_f H_2O + \Delta H_f CO) - (\Delta H_f TNT)]$$

$$\therefore Q = [(2.5 \times (-241.8) + 3.5 \times (-110.5)) - (-26.10)]$$

$$\therefore Q = [(-991.25) - (-26.10)] = -965.15 \text{ kJ mol}^{-1}$$

$$MW_{\text{TNT}} = [84.077 + 5.040 + 42.021 + 95.994] = 227.132 \text{ g mol}^{-1}$$

$$\therefore Q = \frac{\Delta H_f \times 1000}{MW} = \frac{(-965.15 \times 1000)}{227} = -4251 \text{ kJ kg}^{-1}$$

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Ref: [6], [8]

Figure 9 – Thermochemistry of CHNO Explosives

Using elemental composition and product rules, such as the Kistiakowsky–Wilson and modified Kistiakowsky–Wilson schemes, balanced detonation equations can be written. These, combined with tabulated heats of formation, give the heat of explosion Q in $\text{kJ}\cdot\text{kg}^{-1}$. This value defines the chemical energy available to raise the product temperature and pressure and to provide $P\Delta V$ work [9]. Thermochemical results are then used as inputs to product gas equations of state, such as JWL, and to hydrocode models that predict blast loading, case fracture, and fragment velocity for a given munition design [10].

6. From chemistry to Munition Design

Figures 10 and 11 showed how these principles map onto the components of the munition. Sensitivity and critical diameter were associated with the fuze, which must turn a small initiating stimulus into a reliable detonation in the main fill while remaining safe in storage and handling. Heat of formation, oxygen balance, detonation velocity, and critical diameter were associated with the main fill, which must generate enough pressure and energy to fragment the body within the space allowed by the system geometry. Heat of combustion, burn rate law, and gas equations of state were associated with the tail propellant, which must deflagrate in a controlled manner to launch the weapon without structural failure and without unintended transition to detonation.

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Chemistry to Physics Linkages

Sensitivity & critical diameter (chemical structure → initiation physics)

- Molecular structure, formulation and microstructure set how easily an explosive responds to impact, friction, heat and shock.
- These same factors control the critical diameter – the smallest charge size that can sustain a detonation instead of quenching.
- Together they define whether a given explosive will actually support a stable detonation wave in the geometry the designer wants.

Confinement & geometry (charge layout → pressure and fragmentation)

- Casings, liners and surrounding structures constrain expansion, turning chemical energy into pressure histories that drive case fracture.
- Charge shape and wall thickness influence wave focusing, fragment mass and spray pattern.
- So, the way the chemistry is packaged decides how the physics of the blast and fragmentation actually look.

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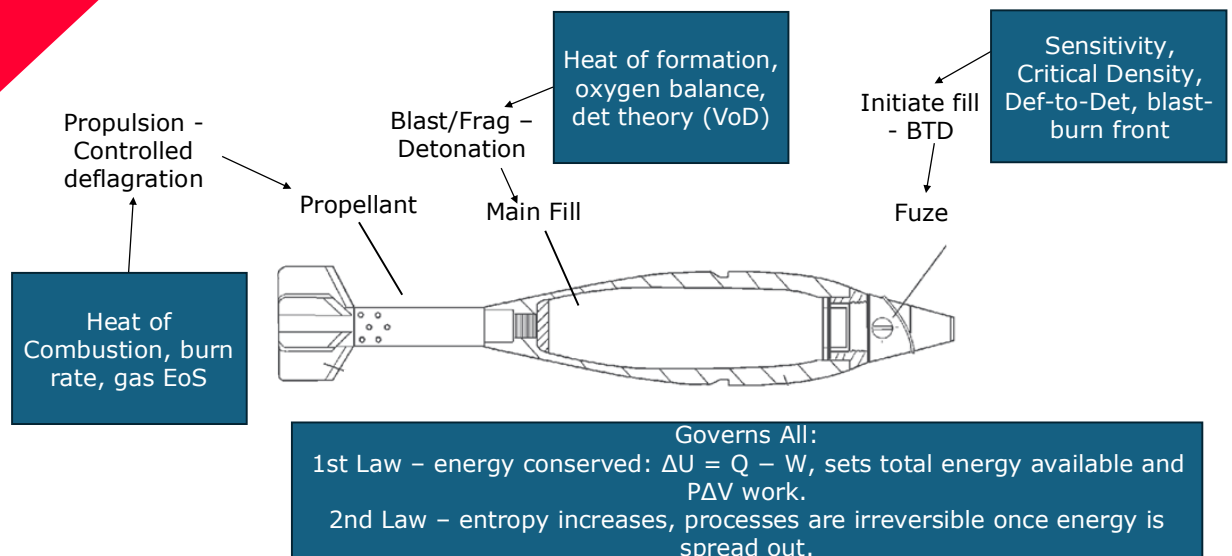
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Ref: [5], [9]

Figure 10 – Chemistry to Physics Linkages

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From Chemistry to Munition Design



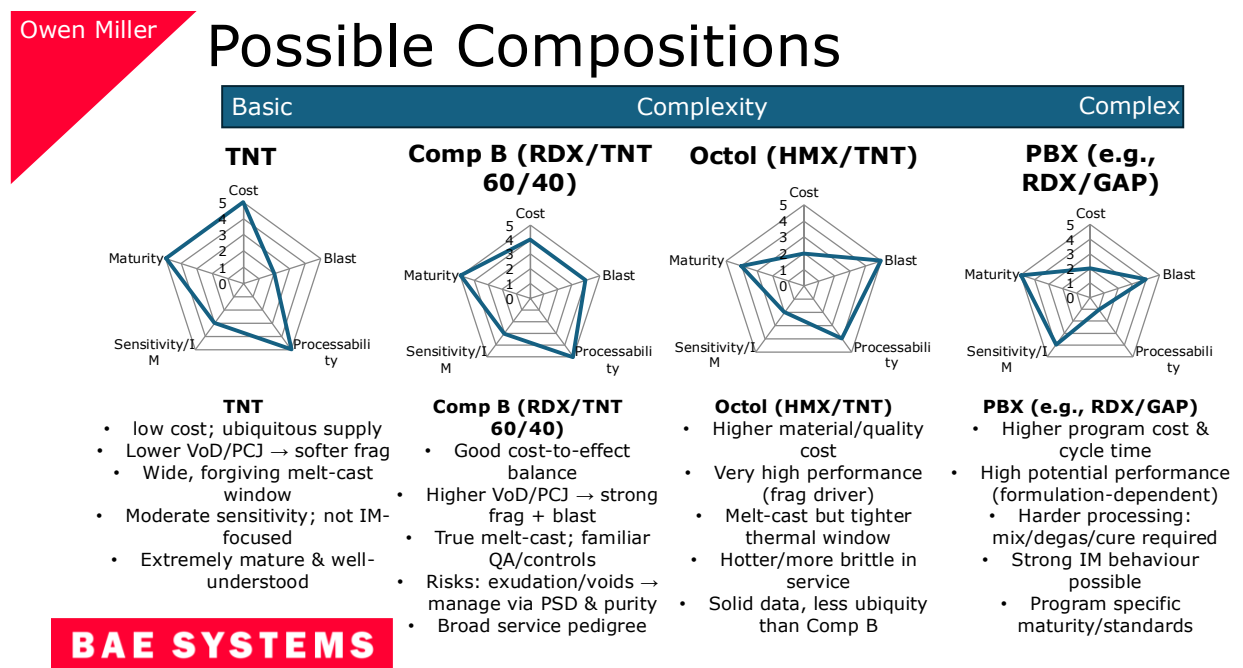
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Ref: [5], [10]

Figure 11 – From Chemistry to Munition Design

Candidate fills were compared in Figure 12, including TNT, Composition B, Octol, and polymer bonded explosive formulations. Higher RDX or HMX content generally increases density and specific energy, which increases detonation velocity and detonation pressure. However, higher crystal energy and different microstructures can increase sensitivity and reduce tolerance to high acceleration launch environments [11]. TNT based fills therefore remain attractive for many gun launched munitions due to robust processing and survivability under launch, even when higher performance formulations exist [12].



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Figure 12 – Possible Compositions

7. So What?

The original question asked how chemical principles govern the lifecycle of energetic materials. From a design and energy release perspective, those principles define the design envelope for munition effectiveness.

Thermodynamics constrains the total energy budget and direction of change through relations such as $\Delta U = Q - W$. Thermochemistry, oxygen balance, and kinetics define how much energy can be released, which products are formed, and how quickly release occurs, which then governs pressure generation and $P\Delta V$ work. Sensitivity, critical diameter, confinement, and coupling determine whether release proceeds as controlled deflagration or detonation, and therefore whether the required blast and fragmentation outputs are achieved within safety and insensitive munitions limits.

Real behaviour deviates from idealised theory due to geometry, manufacturing variation, ageing, and model assumptions. The same chemistry that governs energy release also influences stability and degradation, so design choices affect storage, demilitarisation, and environmentally compliant disposal.

8. Conclusion

This concludes that ideal behaviour implied by theory is rarely observed in full. Real systems are constrained by weapon system, available mass and volume for energetic material, cost, safety policy, manufacturing capability, and demilitarisation routes. The design question is typically framed as follows: The space and mass available for

energetic fill are fixed and a required performance level is specified, the formulation and configuration that will deliver that performance must then be selected while remaining compliant with mechanical constraints, safety requirements, and lifecycle limits.

Thermochemical calculations, equations of state, TNT equivalence, and empirical warhead design curves provide the technical basis for this selection, but survivability under launch, ageing behaviour, insensitive munitions compliance, and disposal feasibility must also be accommodated.

This results that chemical principles do not only describe energy release, they set the outer bounds of what is physically achievable for a given warhead concept. Within those bounds, engineering judgement and system constraints determine the compromise between performance, robustness, and lifecycle burden. In that sense the chemistry of energetic materials governs not only how a munition functions in analysis, but also how its design is shaped to remain effective, safe, and manageable throughout its lifecycle.

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9. References

- [1] BAE Systems, “81mm mortar ammunition,” BAE Systems, [Online]. Available: <https://www.baesystems.com/en-uk/product/81mm-mortar-ammunition>. [Accessed 30 12 2026].
- [2] R. M. L. T. G. A. S. T. Jeffrey Lewis, “Quantifying the Transport of Energetic Materials in Unsaturated Sediments from Cracked Unexploded Ordnance,” *Journal of Environmental Quality*, vol. 38, no. 6, pp. 2229-2236, 2009.
- [3] M. A. B. Yunus A. Çengel, Thermodynamics: An Engineering Approach, New York: McGraw Hill Education, 2019.
- [4] Engineer Design handbook. Warheads-general, vol. 1, Alexandria: Army Materiel Comman Alexandria VA, 1964, p. 38.
- [5] J. d. P. Peter William Atkins, Atkins’ Physical Chemistry, Oxford: Oxford University Press, 2018.
- [6] N. K. Bourne, “On the critical threshold for detonation,” *Combustion and Flame*, vol. 244, 2022.

- [7] W. C. D. Wildon Fickett, Detonation: Theory and Experiment, Berkeley, California: Courier Corporatio, 2000.
- [8] T. URBANSKI, Chemistry and Technology of Explosives, vol. 1, I. Jeczalikowa, Ed., Oxford: PWN-POLISH SCIENTIFIC PUBLISHERS, 1964.
- [9] L. E. L, “Adiabatic Expansion Of High Explosive Detonation Products,” University of California, Livermore, 1968.
- [10] C. L. Mader, Numerical Modeling of Explosives and Propellants, Second Edition, vol. 2, 1997.
- [11] NATO, “Manual of Nato Safety Principles for the Storage of military Ammunition and Explosives - AASTP-1,” Allied Ammunition Storage and Transport Publications, 2010.
- [12] NATO, “Guidance on the Assessment and Development of Insensitive Munitions,” Nato Standardization Agency, 2010.

10. Appendix A – Design Slide Pack

Energetic Material Lifecycle Chemistry

Presented By:

Owen Miller (2221022), Libbie Bush (2223155),
Charles Hadley (2207149) & Dan Garton (2219350)

For Group Presentation in Advanced Chemistry of OME (ACDA6020)

The BAE SYSTEMS logo, with the text "BAE SYSTEMS" in white capital letters on a red rectangular background.

The Question

1. Energetic Material Lifecycle Chemistry – From Synthesis to Demilitarisation (4 people)

Critically evaluate how chemical principles govern the entire lifecycle of key energetic materials, from synthesis and energy release to degradation and environmentally compliant disposal.

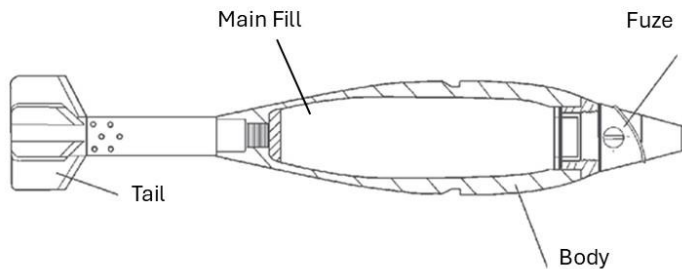
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Munition Life Cycle



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The Munition: 81mm Mortar



A typical 81mm Mortar will be used as the example throughout this lifecycle presentation.

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Design

How do chemical principles govern energy release that effect munition design?

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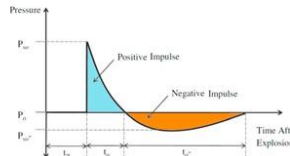
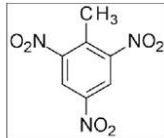
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Laws of Thermodynamics in Energetics

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chemical energy → heat → pressure → mechanical work.



Understanding these laws is essential for:

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Ref: [1], [2]

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First Law of thermodynamics:
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In an explosive event, chemical bond energy is converted into internal energy; expanding gases then perform mechanical work on the case and the air.

For gas expansion against external pressure: a large increase in volume at high pressure gives a large amount of work available for blast and fragmentation.

Example: 81mm Mortar TNT, energy left once case has fragmented

$$Wb = 1.19 \left[\frac{1 + Mr(1 - Mc)}{1 + Mr} \right] C$$

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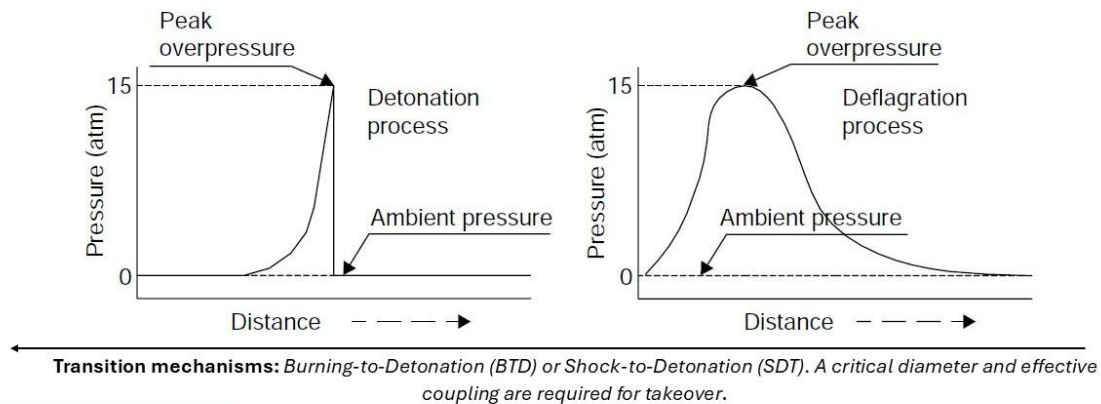
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Detonation vs Deflagration

Detonation: Supersonic, shock-supported reaction front; energy transfer via compression waves; near-constant VoD for a given explosive and density.

Deflagration: Subsonic surface reaction; heat/pressure diffusion governs rate. Confinement increases burn speed but no internal shock.



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Ref: [4], [5]

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Second Law, Entropy & Explosive Efficiency

the total entropy, or disorder, of a closed system can only increase over time



$$\Delta S = \text{Entropy} = \frac{\Delta Q}{T}$$

- Heat flows naturally from the hot block to the cold block.
- As this happens, energy that was concentrated in the hot block becomes more spread out between both blocks.
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Oxygen Balance & Product Composition

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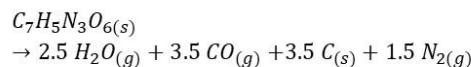
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- Fuel-rich explosives: slightly lower flame temperature, more soot and CO, often reduced sensitivity and good casting behaviour.
- Near-zero or slightly positive OB formulations: hotter, cleaner gases and higher performance, but usually more sensitive.

Example: TNT

Products of TNT – $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$



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Ref: [2], [7]

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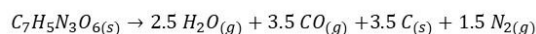
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- Comparing Q ($\text{kJ}\cdot\text{kg}^{-1}$) between explosives allows the rank of fills by energy density and see what extra performance we gain over TNT.
- The same thermochemical data feed into EOS and hydrocode models, so this is the link from molecular structure $\rightarrow$ predicted blast and fragmentation.

Table 5.5 Modified Kistiakowsky–Wilson rules

Rule no.	Conditions
1	Hydrogen atoms are converted to water
2	If any oxygen remains then carbon is converted to carbon monoxide
3	If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4	All the nitrogen is converted to nitrogen gas, N_2

Product Energy Outputs	
Compound	ΔH_f (kJ/mol)
TNT _(s)	-26.10
RDX _(s)	+62.00
C _(s)	00.00
CO _{2(g)}	-393.50
CO _(g)	-110.50
H ₂ O _(g)	-241.80
N _{2(g)}	00.00
O _{2(g)}	00.00



$$\therefore Q = [(\Delta H_f \text{Products}) - (\Delta H_f \text{Reactants})]$$

$$\therefore Q = [(\Delta H_f \text{H}_2\text{O} + \Delta H_f \text{CO}) - (\Delta H_f \text{TNT})]$$

$$\therefore Q = [(2.5 \times (-241.8)) + (3.5 \times (-110.5)) - (-62.10)]$$

$$\therefore Q = [(-991.25) - (-26.10)] = -965.15 \text{ kJmol}^{-1}$$

$$MW_{\text{tnt}} = \left[\underset{\text{C}}{84.077} + \underset{\text{H}}{5.040} + \underset{\text{N}}{42.021} + \underset{\text{O}}{95.994} \right] = 227.132 \text{ g mol}^{-1}$$

$$\therefore Q = \frac{\Delta H_f \times 1000}{MW} = \frac{(-965.15 \times 1000)}{227} = -4251 \text{ kJkg}^{-1}$$

Ref: [6], [8]

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Chemistry to Physics Linkages

Sensitivity & critical diameter (chemical structure → initiation physics)

- Molecular structure, formulation and microstructure set how easily an explosive responds to impact, friction, heat and shock.
- These same factors control the critical diameter – the smallest charge size that can sustain a detonation instead of quenching.
- Together they define whether a given explosive will actually support a stable detonation wave in the geometry the designer wants.

Confinement & geometry (charge layout → pressure and fragmentation)

- Casings, liners and surrounding structures constrain expansion, turning chemical energy into pressure histories that drive case fracture.
- Charge shape and wall thickness influence wave focusing, fragment mass and spray pattern.
- So, the way the chemistry is packaged decides how the physics of the blast and fragmentation actually look.

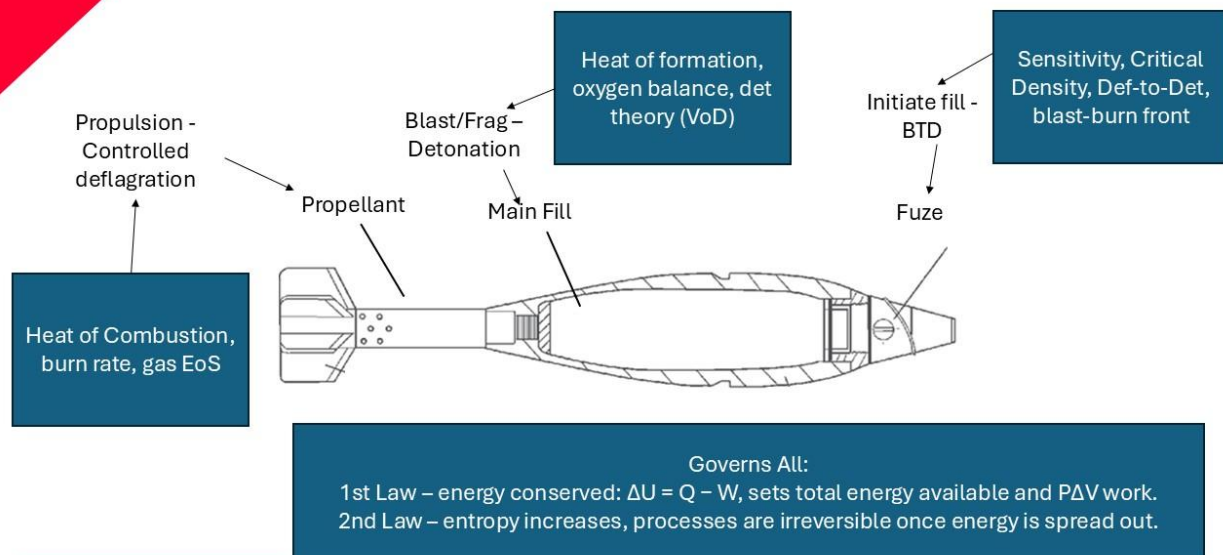
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Ref: [5], [9]

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From Chemistry to Munition Design



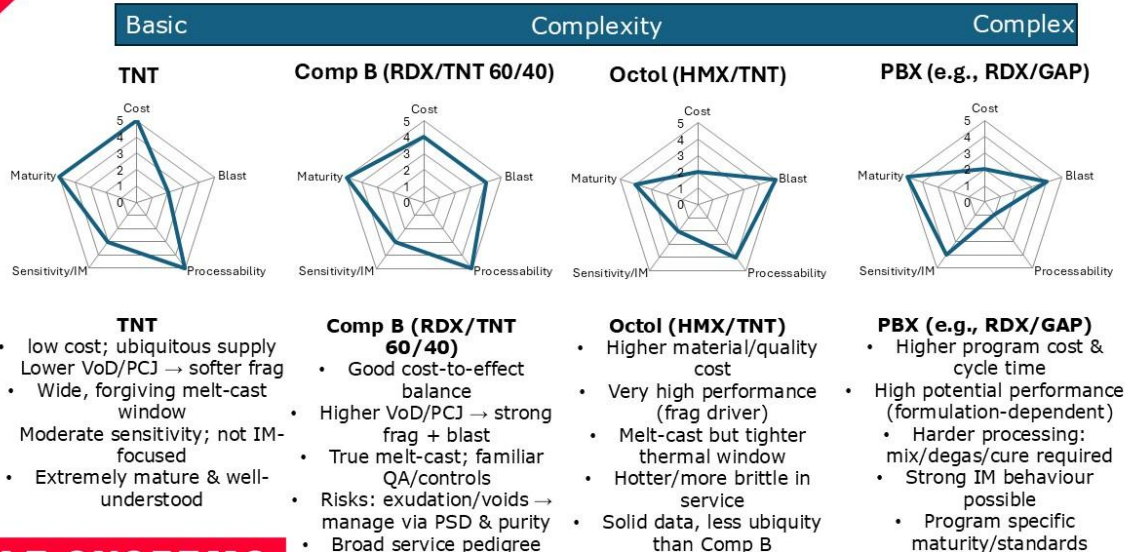
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Ref: [5], [10]

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Possible Compositions



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Ref: [11], [12]

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So What?

- Chemical principles set the design envelope: ΔH^f , oxygen balance, kinetics, sensitivity and EOS fix how much energy a fill can release, at what rate, and in which mode (burn, deflagration, detonation).
- Engineering works inside that envelope: case geometry, confinement and explosive train tune how much of that energy becomes useful blast/fragmentation versus other channels, balancing performance against safety and IM requirements.
- Models have limits: TNT-style thermochemistry, constant-P/constant-V assumptions and ideal product rules are approximations – real munitions see non-ideal products, gradients, manufacturing variation and ageing.
- Lifecycle link: the same chemistry that governs energy release also controls stability, degradation pathways and toxic products, so choices made at design must support safe storage, use, demilitarisation and environmentally compliant disposal.

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References

- [1] BAE Systems, "81mm mortar ammunition," BAE Systems. [Online]. Available: <https://www.baesystems.com/en-uk/product/81mm-mortar-ammunition>. [Accessed: 30-Dec-2026].
- [2] J. Lewis, R. M. L. Thiboutot, G. Ampleman, and S. Taylor, "Quantifying the Transport of Energetic Materials in Unsaturated Sediments from Cracked Unexploded Ordnance," *Journal of Environmental Quality*, vol. 38, no. 6, pp. 2229–2236, 2009.
- [3] Y. A. Çengel and M. A. Boles, *Thermodynamics: An Engineering Approach*. New York, NY, USA: McGraw-Hill Education, 2019.
- [4] U.S. Army Materiel Command, *Engineering Design Handbook: Warheads—General*, vol. 1. Alexandria, VA, USA: Army Materiel Command, 1964, p. 38.
- [5] P. W. Atkins and J. de Paula, *Atkins' Physical Chemistry*. Oxford, UK: Oxford University Press, 2018.
- [6] N. K. Bourne, "On the critical threshold for detonation," *Combustion and Flame*, vol. 244, 2022.
- [7] W. Fickett and W. C. Davis, *Detonation: Theory and Experiment*. Berkeley, CA, USA: University of California Press, 1979.
- [8] T. Urbanski, *Chemistry and Technology of Explosives*, vol. 1, I. Jęczalikowa, Ed. Oxford, UK: Pergamon Press, 1964.
- [9] E. L. Lee, H. C. Hornig, and J. W. Kury, "Adiabatic Expansion of High Explosive Detonation Products," University of California, Lawrence Radiation Laboratory, Livermore, CA, USA, Rep. UCRL-50422, 1968.
- [10] C. L. Mader, *Numerical Modeling of Explosives and Propellants*, 2nd ed. Boca Raton, FL, USA: CRC Press, 1997.
- [11] NATO, AASTP-1: *Manual of NATO Safety Principles for the Storage of Military Ammunition and Explosives*. Brussels, Belgium: NATO, 2010.
- [12] NATO, AOP-39: *Guidance on the Assessment and Development of Insensitive Munitions*. Brussels, Belgium: NATO Standardization Agency, 2010.

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