

From Formulation Composition to Chemical Energy Release

Session 2: Thermochemistry of Energetic Materials

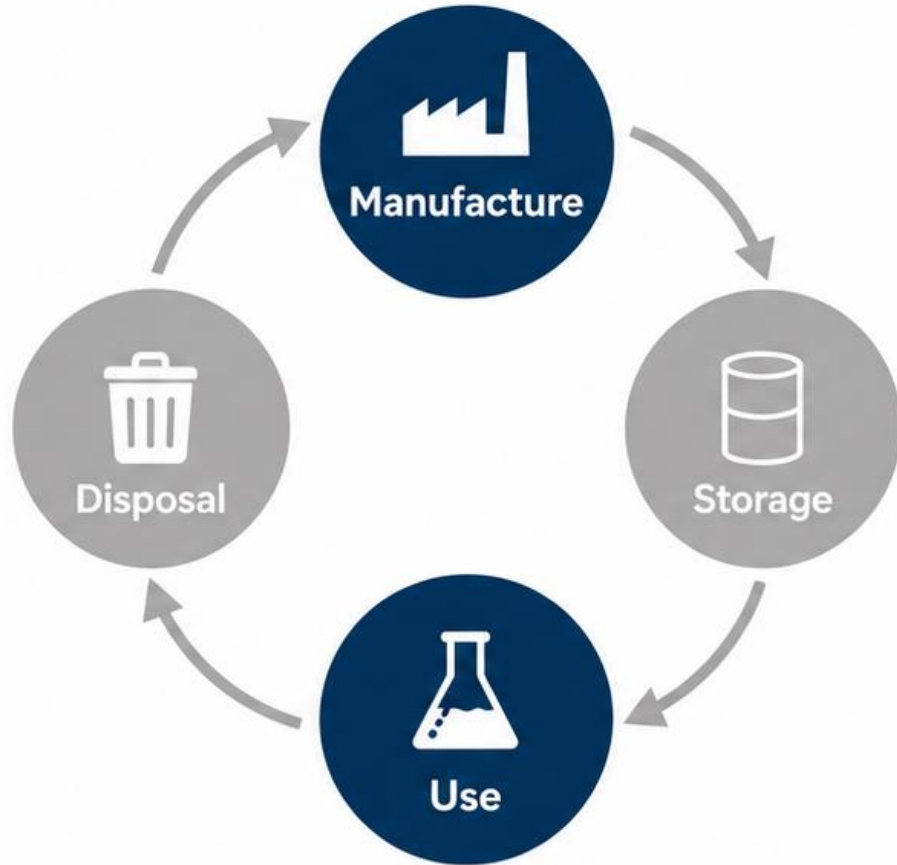


Session plan

From formulation composition to useful work:
how chemistry and thermodynamics link to modern OME materials.

- 1 Energy accounting** — Where does reaction energy go?
- 2 Reaction enthalpy** — How do we quantify chemical energy change?
- 3 Oxygen balance and formulations** — How does composition affect oxygen availability?
- 4 Products and heat release** — How do product assumptions affect energy release?
- 5 Useful work** — How is chemical energy delivered in a system?
- 6 Synthesis and key takeaways** — What do these ideas mean for modern OME materials?

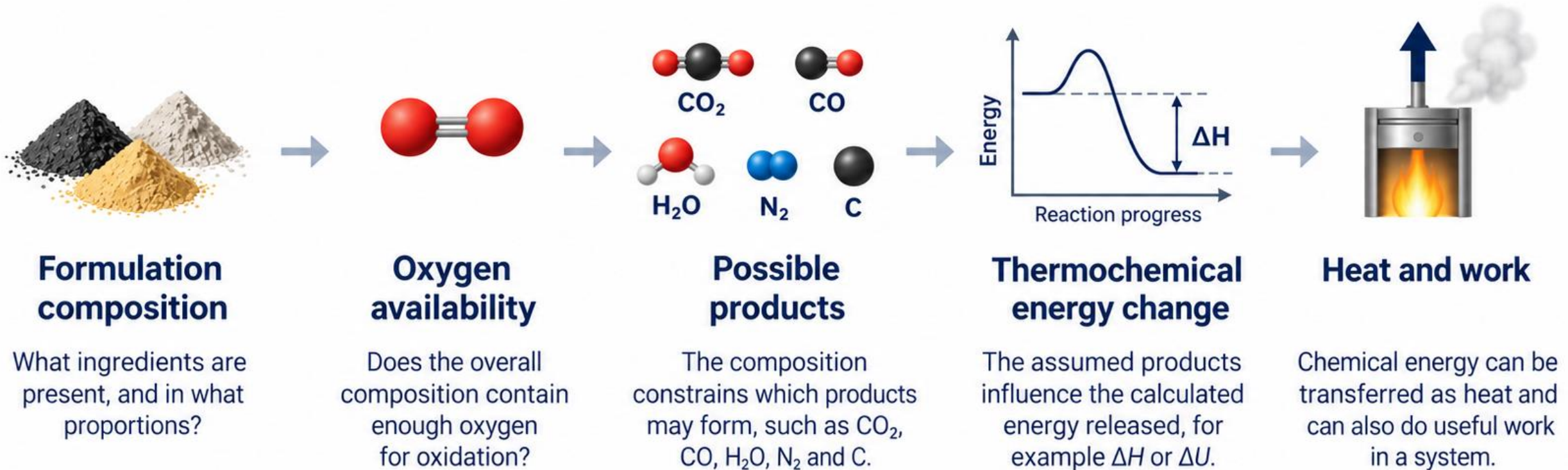
Where are we in the OME lifecycle?



How does composition determine energetic potential during use?

S2 focus: Manufacture determines composition → composition constrains chemistry → chemistry determines energetic potential.

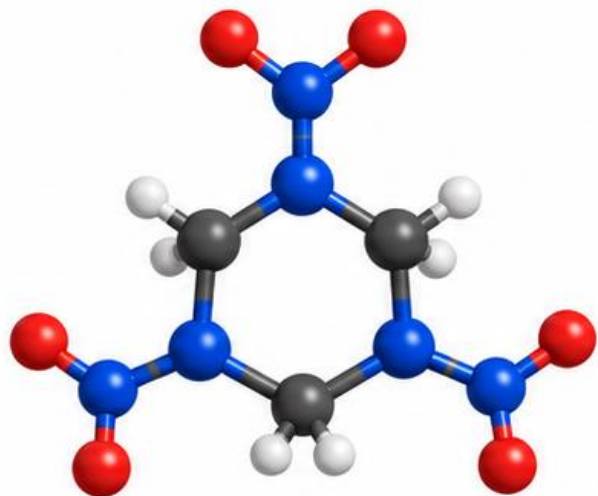
From composition to energetic potential



Manufacture determines composition; composition constrains chemistry; chemistry determines energetic potential during use.

What leaves manufacture?

Single energetic compound



Defined molecular composition

Energetic formulation



Overall behaviour depends on the combined composition

Composition determines the atoms available for reaction

For thermochemical analysis, we must know what is actually present — not just the name of the energetic ingredient.

Modern energetic materials – three design challenges



Modern pyrotechnics

- Deliver the required heat, light and reaction products
- Reduce problematic ingredients and emissions



Green propellants

- Balance energy and gas generation with lower toxicity
- Consider handling, compatibility and environmental impact



Modern explosive materials

- Balance energetic potential with stability and reduced sensitivity
- Molecular and formulation design both matter

**Different applications — the same chemical question:
how does composition determine energy release and products?**

Part 1:

Energy accounting — the thermodynamic language

1

Define the thermodynamic framework

- System, surroundings and boundary

2

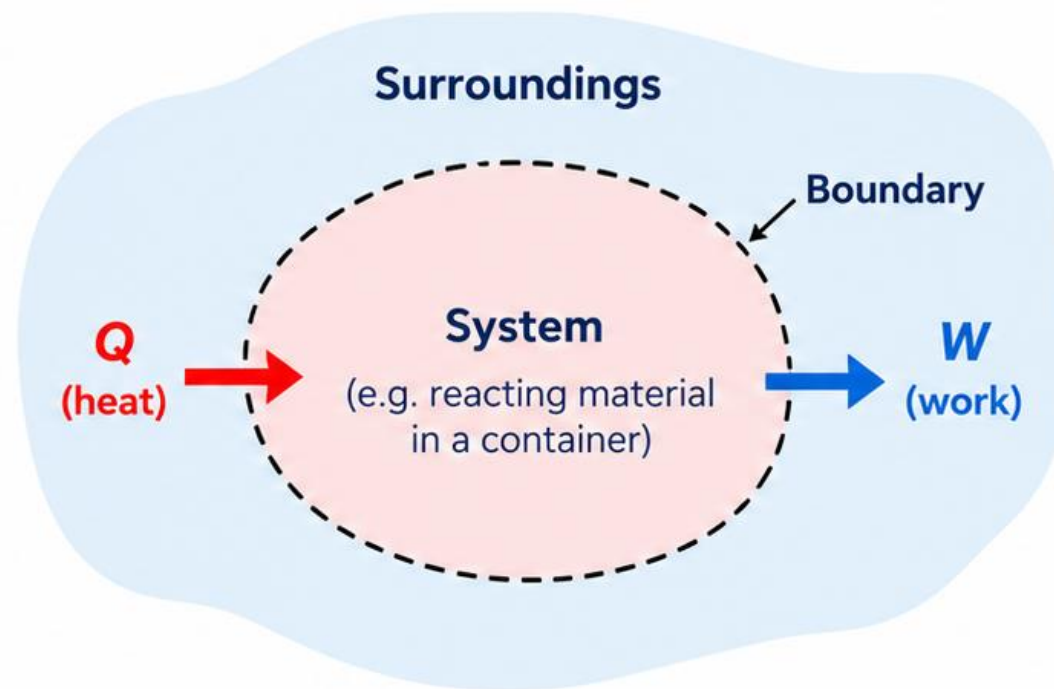
Introduce energy terms

- Internal energy, heat and work

3

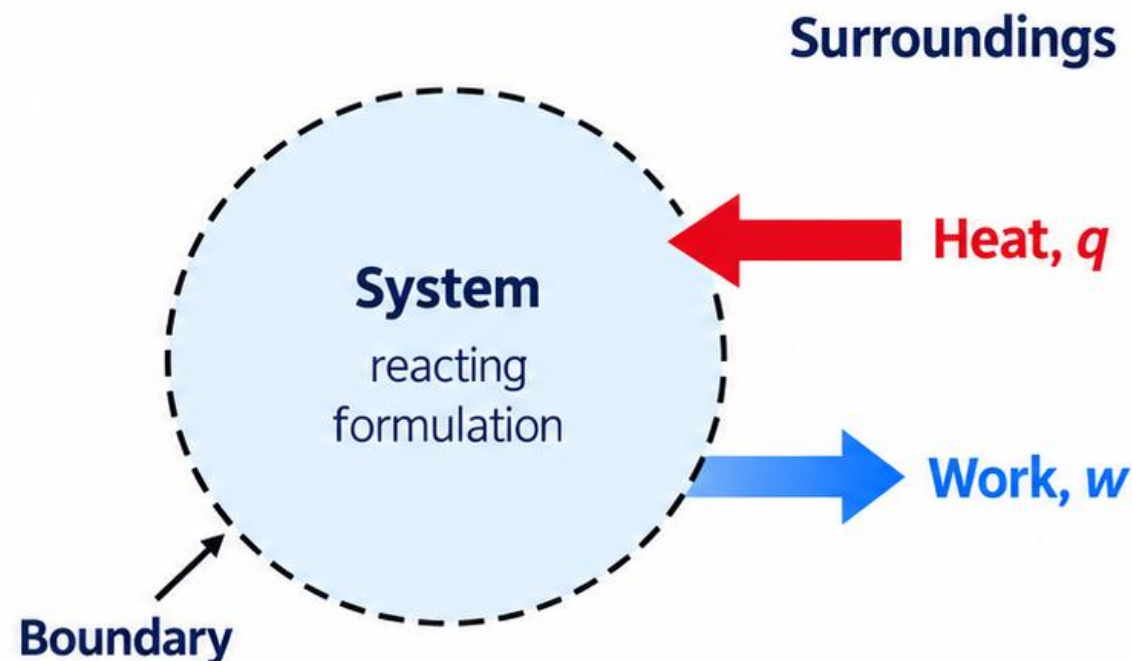
Apply the First Law

- Energy balance for a closed system
- Enthalpy and the relationship between ΔU and ΔH



What is thermodynamics?

- Thermodynamics studies **energy changes** and **energy transfers** in systems.
- It helps us relate the **chemical energy** of a formulation to the **heat** and **work** released during reaction.
- In this session we use thermodynamics to define heat, work, internal energy (U) and enthalpy (H).

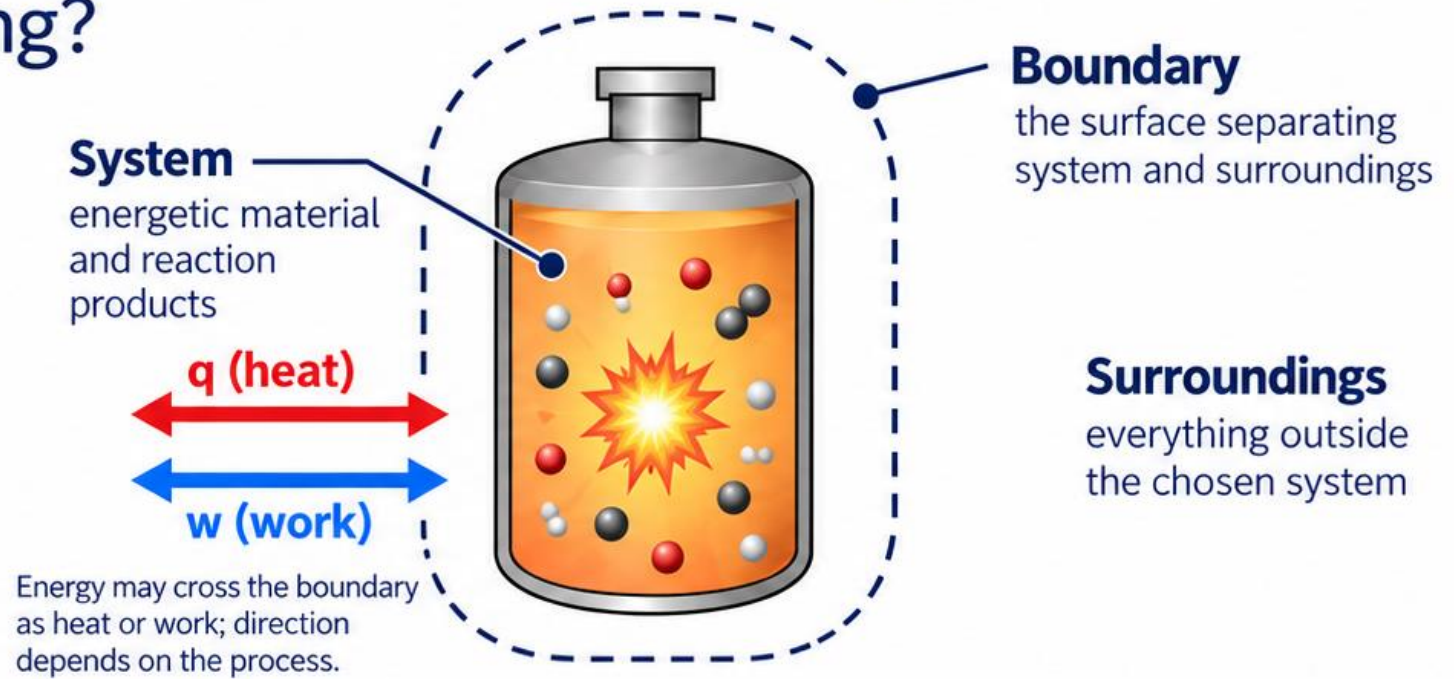


Thermodynamics gives us the framework to connect formulation composition, reaction chemistry, heat and work.

System, surroundings and boundary

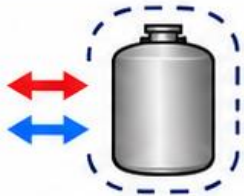
What exactly are we analysing?

- **System:** the part of the universe chosen for study
- **Surroundings:** everything outside the system
- **Boundary:** the surface separating system and surroundings
- **Universe** = system + surroundings



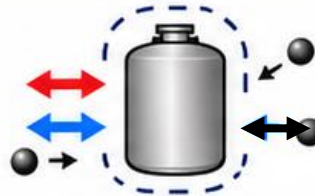
Closed system

energy may cross;
matter does not



Open system

energy and matter
may cross



Isolated system

neither energy
nor matter crosses



The choice of system boundary determines how we describe and account for energy transfer.

How do we describe the state of a system?

A thermodynamic state is defined by measurable properties.

State variables

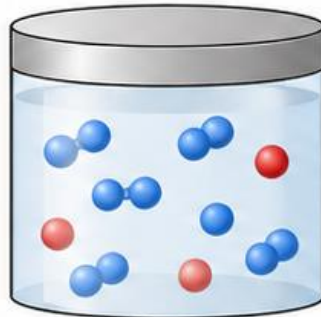
- pressure, p
- volume, V
- temperature, T
- composition, n_i

Internal energy, U

- a property of the system state
- Changes when the state changes
- Depends only on the initial and final states (U is a state function)

State 1

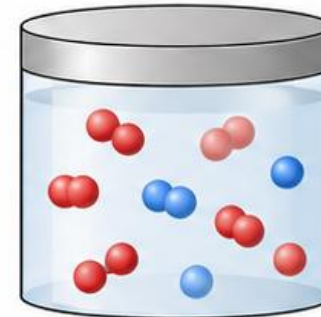
- reactant-rich
- lower T / lower p



$T_1, p_1, V_1, n_{i,1}$

state change

$$\Delta U = U_2 - U_1$$



$T_2, p_2, V_2, n_{i,2}$

State 2

- product-rich
- higher T / higher p

U is a state function. ΔU depends only on the initial and final states, not on the path taken.

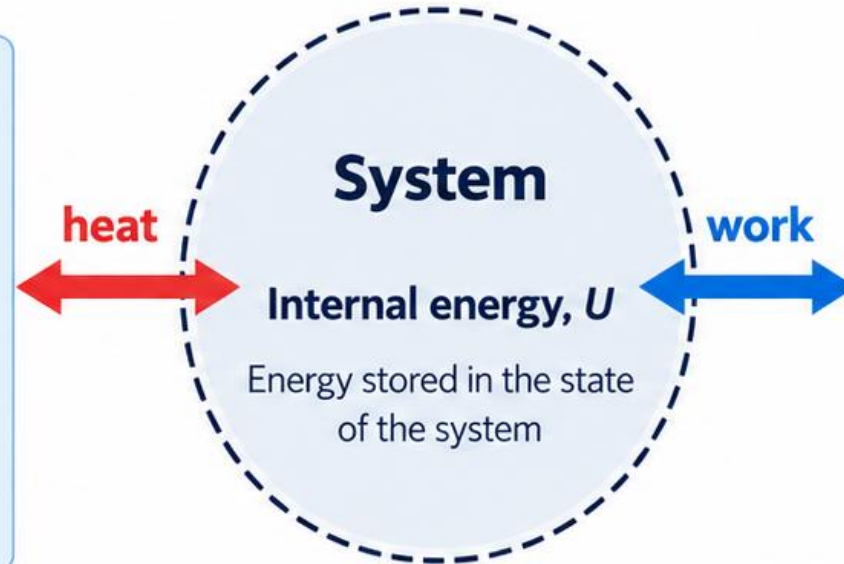
Thermodynamics compares states of a system; when the state changes, the internal energy can change.

Heat and work: how energy crosses the boundary

Internal energy is a property of the system; heat and work describe energy transfer during a process.

Heat, q

- Energy transferred because of a temperature difference
- $q > 0$: heat enters the system
- $q < 0$: heat leaves the system



Work, w

- Energy transferred when a force acts through a distance
- In OME, often due to gas expansion
- $w > 0$: work done on the system;
 $w < 0$: work done by the system

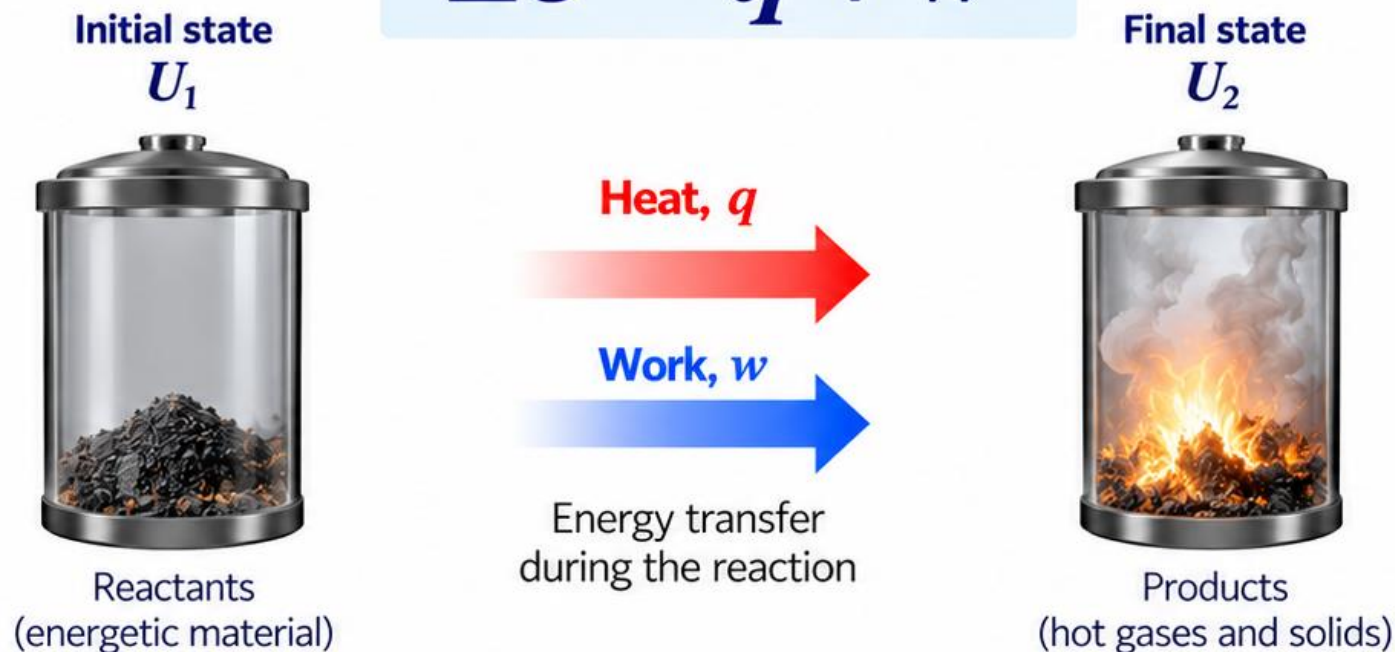
State function: U | Path-dependent quantities: q and w

Heat and work are not stored in the system — they are modes of energy transfer across the boundary.

First Law of Thermodynamics

A **change** in the **internal energy** of a system must be accounted for by heat and/or work transfer.

$$\Delta U = q + w$$



Heat, q

- Energy transferred because of a temperature difference.
- $q > 0$: heat enters the system.
- $q < 0$: heat leaves the system.

Work, w

- Energy transferred when a force acts through a distance.
- $w > 0$: work is done on the system.
- $w < 0$: work is done by the system.

Sign convention

- q and w are positive when energy enters the system.
- q and w are negative when energy leaves the system.

Key points

- The First Law of Thermodynamics is an energy balance.
- A change in internal energy must be accounted for by heat and/or work transfer.
- For an energetic material, the chemical reaction changes the internal energy of the system.
- Energy may leave as heat and/or as work (e.g. expansion of gases).
- The First Law does not tell us whether a reaction will occur or how fast it will proceed.

Remember:

- Internal energy, U , is a property of the state (state function).
- Heat, q , and work, w , are energy transfers during a process (path-dependent quantities).

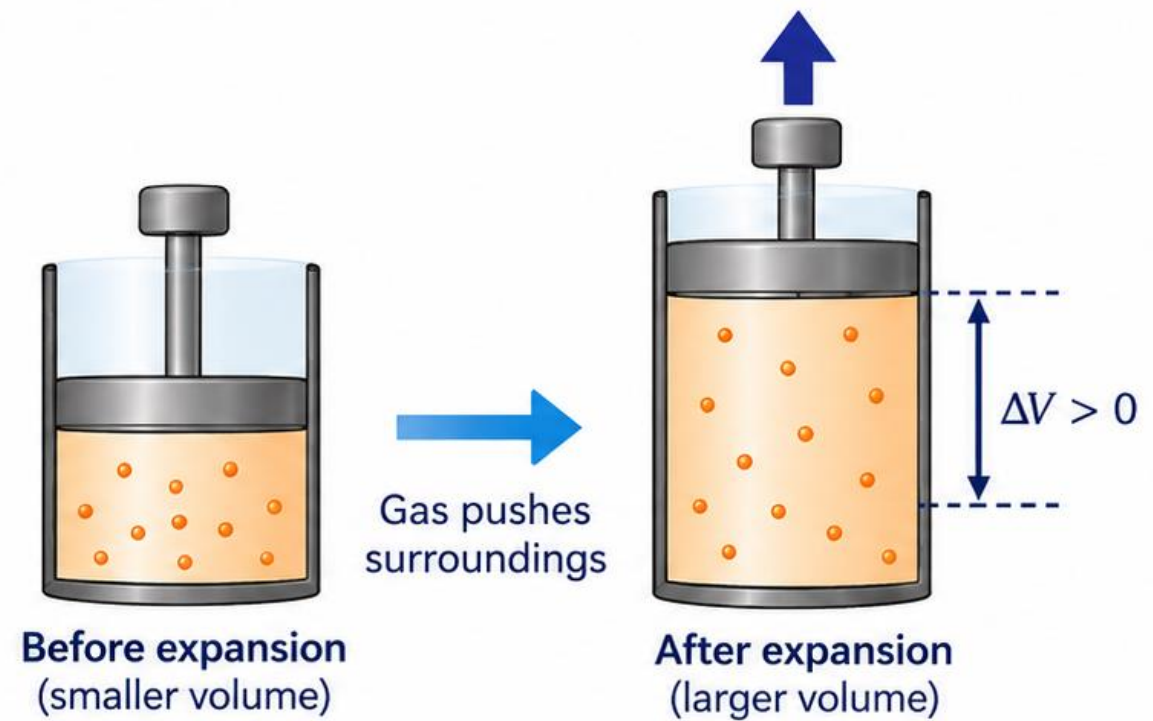
Expansion work

When gases push the surroundings

$$w = - \int p_{\text{ext}} dV$$

For constant external pressure:

$$w = - p_{\text{ext}} \Delta V$$



Interpretation

- **Expansion:** $\Delta V > 0 \rightarrow w < 0$ (system does work on surroundings)
- **Compression:** $\Delta V < 0 \rightarrow w > 0$ (surroundings do work on system)

In energetic-material reactions, rapidly generated gases can do expansion work on a projectile, casing, piston or the surrounding atmosphere.

Pressure alone is not work. Work requires a change in volume (or displacement) against an external pressure.

Why introduce enthalpy?

If internal energy already describes the energy of a system, why do chemists also use **enthalpy**?

$$H = U + pV$$

Rigid container (constant volume)

- Volume is fixed ($\Delta V = 0$).
- No expansion work ($w = 0$).
- Change in internal energy is the relevant quantity.



$$q = \Delta U \quad (\text{at constant volume})$$

Movable boundary (constant pressure)

- Volume can change.
- System expands against an external pressure (e.g. atmosphere or a piston).
- The enthalpy change conveniently accounts for the internal energy change and the expansion work.



$$q = \Delta H \quad (\text{at constant pressure})$$

Key points

- $H = U + pV$ (enthalpy).
- $\Delta H = \Delta U + \Delta(pV)$.
- U and H are state functions.
- Enthalpy is particularly useful when reactions occur at constant pressure, where expansion work is important (e.g. open systems, atmosphere, explosive reactions).

Interpretation

- U describes the internal energy of the system.
- H includes the internal energy and the pV term, which accounts for the work associated with changing volume against an external pressure.
- Enthalpy does not represent a different kind of energy stored in the material; it is a convenient thermodynamic accounting function.

When does heat equal ΔU or ΔH ?

Under specific conditions, the heat transferred equals the change in a state function.

Constant volume ($V = \text{constant}$)



Rigid container

- Volume is fixed ($\Delta V = 0$)
- No pV expansion work
- If no other work occurs:

$$q_V = \Delta U$$

Constant pressure ($p = \text{constant}$)



Movable boundary

- Pressure is constant
- Volume may change
- If pV work is the only work:

$$q_P = \Delta H$$



These are thermodynamic conditions, not labels for explosives or propellants.

Real energetic-material reactions need not remain at constant volume or constant pressure.

q_V and q_P are heat transfers measured under specified conditions.

How are ΔH and ΔU related?

The difference between enthalpy and internal energy arises from the pV term.

Definition of enthalpy

$$H = U + pV$$

Change in a process

$$\Delta H = \Delta U + \Delta(pV)$$

Ideal-gas reactions at the same temperature

$$\Delta_r H = \Delta_r U + \Delta n_g RT$$

$$\Delta n_g = n_g(\text{products}) - n_g(\text{reactants})$$

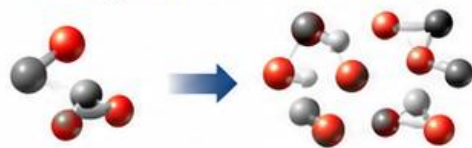
$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T = \text{temperature (K)}$$

(valid for ideal gases, same T)

$$\Delta n_g > 0$$

More gas molecules formed



$$\Delta H > \Delta U$$

(for an exothermic reaction,
 ΔH is less negative)

$$\Delta n_g = 0$$

No change in number of gas molecules

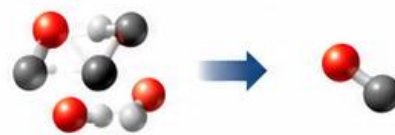


$$\Delta H = \Delta U$$

(at the same temperature)

$$\Delta n_g < 0$$

Fewer gas molecules formed



$$\Delta H < \Delta U$$

(for an exothermic reaction,
 ΔH is more negative)

Numerical example

A reaction produces 4 moles of gas at 298 K.

$$\Delta n_g = +4$$

$$\begin{aligned}\Delta n_g RT &= 4 \times 8.314 \times 298 \\ &\approx 9.9 \text{ kJ mol}^{-1}\end{aligned}$$

If $\Delta U = -500 \text{ kJ mol}^{-1}$, then:

$$\begin{aligned}\Delta H &= \Delta U + \Delta n_g RT \\ &= -500 + 9.9 \\ &\approx -490 \text{ kJ mol}^{-1}\end{aligned}$$

Key point for OME

Changes in the number of gas molecules affect the pV contribution, so ΔH and ΔU may differ. Energetic-material reactions are dynamic and need not occur at constant volume or constant pressure.

Part 2: Reaction enthalpy using chemistry we know

Recalling $\Delta_r H$, $\Delta_f H^\circ$ and Hess's law before applying them to energetic materials.

Reaction enthalpy: connecting thermodynamics to chemistry

Enthalpy is a state function, so the enthalpy change of a reaction can be calculated from the enthalpies of formation of the reactants and products.

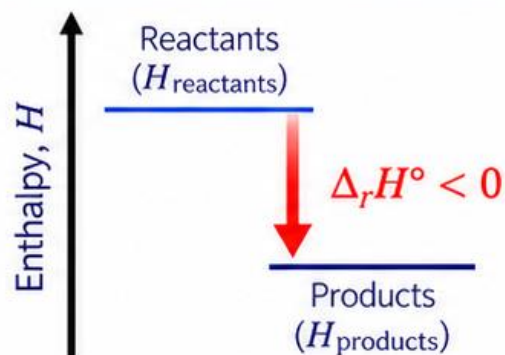
$$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{products}) - \sum \nu \Delta_f H^\circ(\text{reactants})$$

Definitions

- $\Delta_r H^\circ$ Standard enthalpy change of reaction (kJ mol^{-1}).
- $\Delta_f H^\circ$ Standard enthalpy of formation (kJ mol^{-1}): enthalpy change when 1 mol of a compound forms from its elements in their standard states.
- ν Stoichiometric coefficient (from the balanced equation).
- Standard-state conditions: usually 298.15 K and 1 bar (for gases).

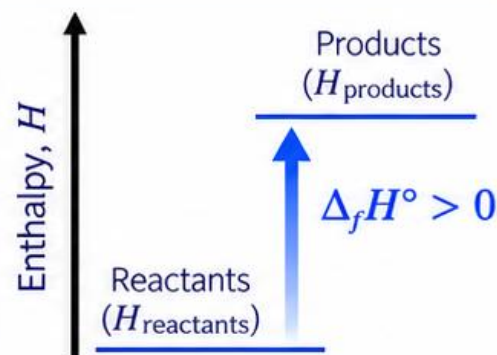
Energy-level diagrams

Exothermic reaction ($\Delta_r H^\circ < 0$)



Products have lower enthalpy than reactants.
Energy is released.

Endothermic reaction ($\Delta_r H^\circ > 0$)



Products have higher enthalpy than reactants.
Energy is absorbed.

Key points

- $\Delta_r H^\circ$ is calculated from standard enthalpies of formation using the balanced chemical equation.
- Enthalpy is a state function, so $\Delta_r H^\circ$ can be determined from initial and final states without knowing the reaction pathway.
- The sign of $\Delta_r H^\circ$ indicates whether the reaction is exothermic (negative) or endothermic (positive).
- The calculated value depends on the assumed products in the reaction equation.

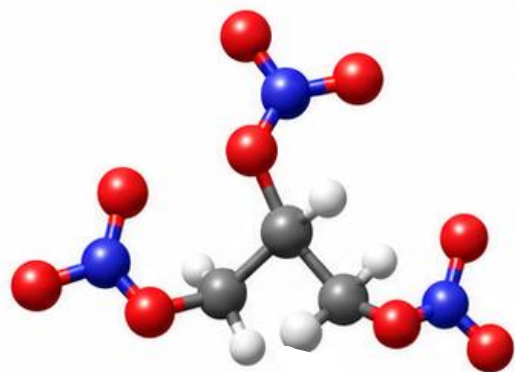
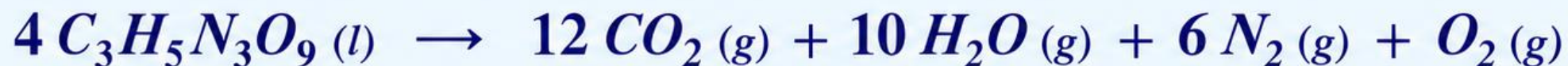
Relevance for OME

- The value of $\Delta_r H^\circ$ belongs to a specified reaction equation — changing the assumed products changes the calculated energy release.
- Accurate identification of the likely products is therefore essential when estimating the energy released by energetic materials.

Retrieval: calculating $\Delta_r H^\circ$ from formation enthalpies

Use standard enthalpies of formation to calculate the enthalpy change for complete decomposition of nitroglycerine.

Reaction (assumed products)



Nitroglycerine
 $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$

Standard enthalpies of formation (298 K, 1 bar)

Species	Formula	$\Delta_f H^\circ$ (kJ mol ⁻¹)
Nitroglycerine (l)	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9 (\text{l})$	-364.0
Carbon dioxide (g)	$\text{CO}_2 (\text{g})$	-393.5
Water (g)	$\text{H}_2\text{O} (\text{g})$	-241.8
Nitrogen (g)	$\text{N}_2 (\text{g})$	0
Oxygen (g)	$\text{O}_2 (\text{g})$	0

Your tasks

- 1** Calculate the standard enthalpy change of reaction, $\Delta_r H^\circ$, for the reaction shown.
- 2** What does the sign of $\Delta_r H^\circ$ tell you about the reaction?
- 3** What assumption have we made about the reaction products?

Calculation

$$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{products}) - \sum \nu \Delta_f H^\circ(\text{reactants})$$

Interpretation

- The negative value of $\Delta_r H^\circ$ represents the energy released per reaction as written (here for 4 mol of nitroglycerine).
- The calculated value depends on the reaction equation and the assumed products.

Part 3: Oxygen balance — from compound to formulation

Oxygen balance: what does it tell us?

Oxygen balance indicates whether the oxygen contained within an energetic material is sufficient for complete oxidation of its carbon and hydrogen content.

For a compound $C_aH_bN_cO_d$:

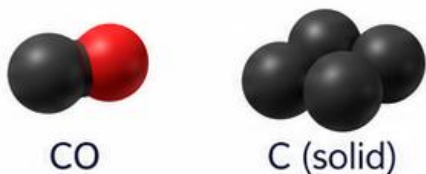
$$\Omega_{CO_2} (\%) = \left[d - 2a - \frac{b}{2} \right] \times \frac{1600}{M}$$

a = number of C atoms
 b = number of H atoms
 c = number of N atoms
 d = number of O atoms
 M = molar mass (g mol^{-1})

Interpretation of oxygen balance

$$\Omega < 0$$

Oxygen-deficient

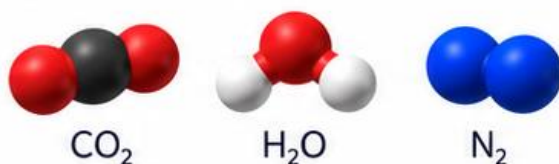


Not enough oxygen for complete oxidation.

More likely to form CO, C and other partially oxidised products.

$$\Omega \approx 0$$

Approximately oxygen-balanced



Approximately sufficient oxygen for complete oxidation of C and H (to CO₂ and H₂O).

$$\Omega > 0$$

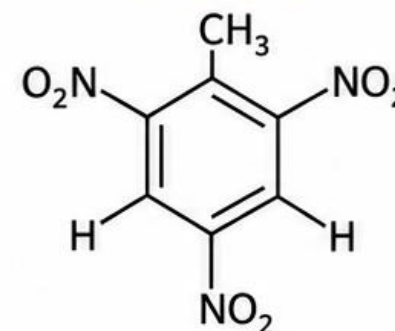
Oxygen-rich



More oxygen than required for complete oxidation.

Oxygen remains in the products (e.g. O₂, NO_x).

Example: TNT



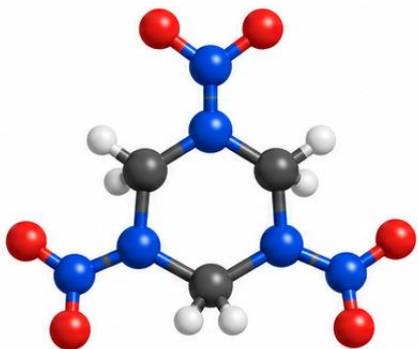
$$\Omega_{CO_2} = -74\%$$

(Klapötke/Kubota)

Oxygen balance describes oxygen availability — it does not uniquely predict the actual reaction products or the energy release.

From a compound to a formulation

Single compound



Example: RDX, $C_3H_6N_6O_6$
one molecule, one formula

- one defined molecular composition
- oxygen balance belongs to that single compound

Formulation

- several chemically different contributors
- oxygen availability depends on the overall composition

80% AP + 20% HTPB



+



80% CL-20 + 20% GAP



+



compound → one composition



formulation → combined composition

For a formulation, oxygen balance is considered for the whole mixture

$$OB_{mix} = \sum w_i OB_i$$

w_i = mass fraction of component i

A formulation cannot be judged by looking at one ingredient alone. Oxygen availability must be considered for the whole formulation.

Oxygen balance of a formulation

For a formulation, the overall oxygen balance is obtained from the mass-weighted contributions of its components.

$$\Omega_{mix} = \sum w_i \Omega_i$$

w_i = mass fraction of component i

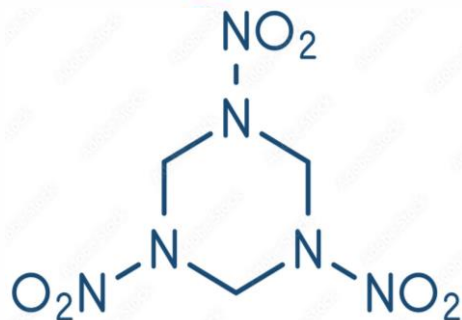
Ω_i = oxygen balance of component i (%)

Example formulation: B-3

60 wt% RDX

$\Omega = -21.6\%$

$C_3H_6N_6O_6$

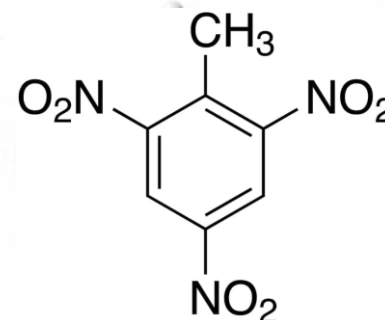


+

40 wt% TNT

$\Omega = -74.0\%$

$C_7H_5N_3O_6$



Oxygen balance of the mixture

$$\begin{aligned}\Omega_{mix} &= 0.60(-21.6) \\ &\quad + 0.40(-74.0) \\ &= \mathbf{-42.6\%}\end{aligned}$$

Formulation oxygen balance depends on both the oxygen balance of each component and the proportion of each component.

This is why manufacture matters: changing formulation composition changes the oxygen available during reaction.

Activity 1: Oxygen balance of real formulations

Calculate and compare the oxygen balance for two energetic material formulations.

$$\Omega_{mix} = \sum w_i \Omega_i$$

w_i = mass fraction of component i

Ω_i = oxygen balance of component i (%)

Formulation A: Composition B-3

60 wt% RDX

$\Omega =$



40 wt% TNT

$\Omega =$



Formulation B: Octol

76 wt% HMX

$\Omega =$



24 wt% TNT

$\Omega =$



Questions

- 1 Calculate the oxygen balance, Ω_{mix} , for Formulation A and Formulation B.
- 2 Which formulation is more oxygen-deficient?
- 3 Based on the oxygen balance, which formulation may be more likely to form CO and/or C (relative to fully oxidised products)? Give a brief reason.
- 4 State one thing you cannot conclude from the oxygen balance alone.

For a compound $C_aH_bN_cO_d$:

$$\Omega_{CO_2}(\%) = \left[d - 2a - \frac{b}{2} \right] \times \frac{1600}{M}$$

a = number of C atoms
 b = number of H atoms
 c = number of N atoms
 d = number of O atoms
 M = molar mass (g mol^{-1})

Which formulation would you expect to have the less oxygen-deficient product mixture — and why?

Activity 1: What do the results tell us?

Calculated oxygen balance for the two formulations.

Formulation A: Composition B-3

60 wt% RDX

$$\Omega = -21.6\%$$

40 wt% TNT

$$\Omega = -74.0\%$$

$$\Omega_{mix} = 0.60(-21.6) + 0.40(-74.0)$$

$$\Omega_{mix} = -42.6\%$$

Formulation B: Octol

76 wt% HMX

$$\Omega = -21.6\%$$

24 wt% TNT

$$\Omega = -74.0\%$$

$$\Omega_{mix} = 0.76(-21.6) + 0.24(-74.0)$$

$$\Omega_{mix} = -34.2\%$$

More oxygen-deficient
(more likely to form CO, C, etc.)



Less oxygen-deficient
(closer to complete oxidation)

Key points

- Both formulations are strongly oxygen-deficient.
- Composition B-3 (−42.6%) is more oxygen-deficient than Octol (−34.2%).
- Based on oxygen availability alone, B-3 would be expected to favour a greater proportion of incompletely oxidised carbon-containing products, such as CO and/or C.

What we cannot conclude from oxygen balance alone

- the actual product distribution
- the exact energy release
- the reaction rate
- the sensitivity
- the overall performance

Mixture oxygen balance is useful for comparing formulations, but it is only one part of the thermochemical picture.

Modern pyrotechnics: composition controls heat and function



Composition
oxidiser + fuel +
functional ingredients



Oxygen availability
depends on overall
formulation composition



Reaction products
e.g. CO₂, H₂O, N₂,
CO, HCl, solid products



Heat output + desired effect
light / colour • smoke • heat • gas

Traditional design question

- What oxidiser/fuel ratio gives the required heat and visible effect?
- How is the desired colour or effect obtained?
- Traditional formulations often used perchlorates and heavy-metal salts.

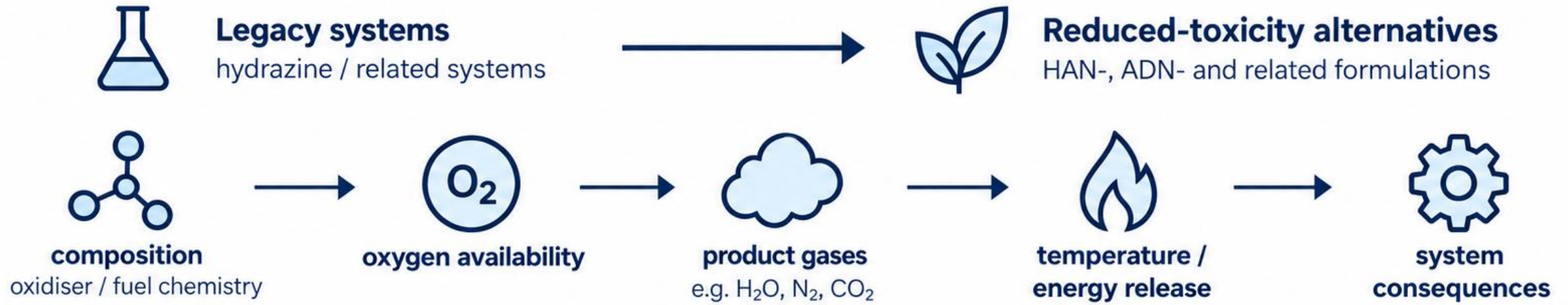
Modern design question

- Can the same function be achieved with less problematic chemistry?
- Reduce perchlorates, heavy metals and smoke.
- Examples: use nitrate or dinitramide oxidisers; high-nitrogen or tetrazolate-based formulations.

Some high-nitrogen materials also gain energetic character from positive enthalpies of formation, not only from oxidation.

Changing the ingredients changes both environmental impact and the thermochemical pathway.

Green propellants: “green” does not mean low-energy



Thermochemical considerations

- Composition determines oxygen availability, gas generation and heat release
- Green does not mean low-energy; performance can remain high
- Thermochemical output must be interpreted alongside formulation design

Formulation selection also considers

- toxicity
- handling and safety
- material compatibility
- environmental impact
- cost / practical deployment

Thermochemical performance must be balanced against safety, handling and lifecycle considerations.

Examples include HAN-, ADN- and HNF-based systems.

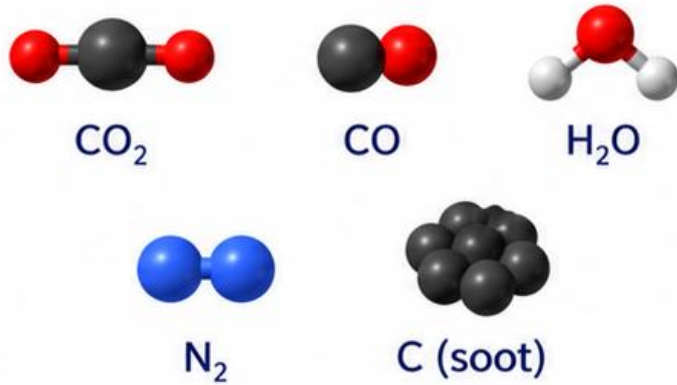
Part 4: Products, heat release and limits of oxygen balance

From oxygen availability to possible products

The oxygen balance of an energetic material influences the types of products that can form.

Oxygen-deficient ($\Omega < 0$)

Not enough oxygen to fully oxidise all fuel elements.



Incomplete oxidation becomes more likely.

Approximately balanced ($\Omega \approx 0$)

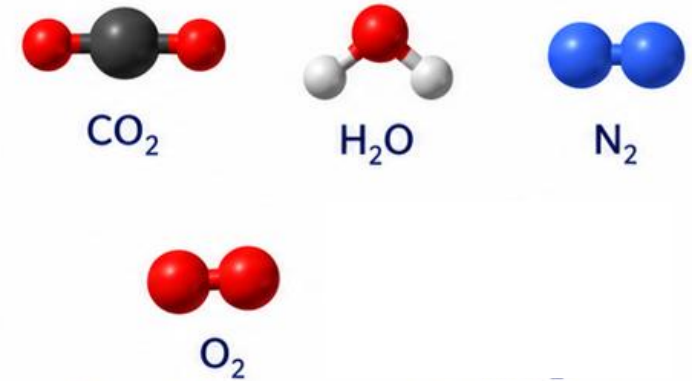
Oxygen is close to the amount needed for complete oxidation.



Main products are CO₂, H₂O and N₂, but other products can still form.

Oxygen-rich ($\Omega > 0$)

More oxygen than required for complete oxidation.



Possible excess oxidising species

Oxygen balance constrains the possible product mixture — it does not uniquely determine it.

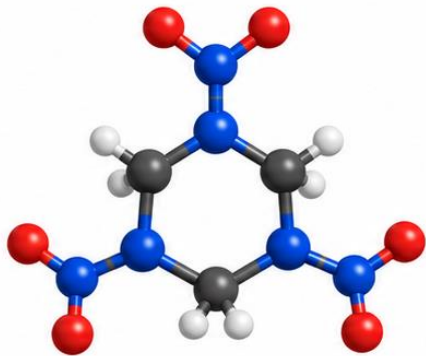
Why do product assumptions change the energy release?

Different products have different standard enthalpies of formation, so different assumed product mixtures give different reaction enthalpies.

$$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{products}) - \sum \nu \Delta_f H^\circ(\text{reactants})$$

Same reactant composition

Example: RDX, $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$

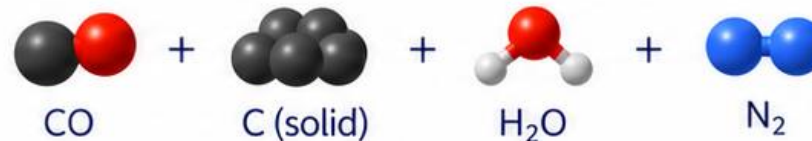


Path A — more complete oxidation



more negative
 $\Delta_r H^\circ$

Path B — more incomplete oxidation



less negative
 $\Delta_r H^\circ$

The thermochemical result depends on the reaction equation we assume.

Oxygen balance helps constrain plausible products, but equilibrium determines the actual product distribution — revisited in S4.

From assumed products to heat release

To estimate the heat released by an energetic formulation, we need to assume chemical products and use formation enthalpies with Hess's law. The calculated value depends on the assumed products.



Example 1: 80% AP / 20% HTPB (by mass)

1 Formulation
80% ammonium perchlorate (AP) (oxidiser)
20% HTPB (fuel / binder)

2 Assumed products (at high temperature)

 CO_2 H_2O N_2 CO C (solid carbon)

3 Hess's law calculation
$$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{products}) - \sum \nu \Delta_f H^\circ(\text{reactants})$$

- Use tabulated standard formation enthalpies, $\Delta_f H^\circ$ (298 K).
- Include stoichiometric coefficients, ν .
- Products and their amounts depend on the assumed product set.

4 Estimated heat of combustion (illustrative)
$$\Delta_r H^\circ \approx -2.0 \times 10^3 \text{ kJ kg}^{-1}$$

(value depends on assumed products and calculation method)

Example 2: 80% CL-20 / 20% GAP (by mass)

1 Formulation
80% CL-20 (energetic oxidiser)
20% GAP (energetic binder)

2 Assumed products (at high temperature)

 CO_2 H_2O N_2 CO C (solid carbon)

3 Hess's law calculation
$$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{products}) - \sum \nu \Delta_f H^\circ(\text{reactants})$$

- Use tabulated standard formation enthalpies, $\Delta_f H^\circ$ (298 K).
- Include stoichiometric coefficients, ν .
- Products and their amounts depend on the assumed product set.

4 Estimated heat of combustion (illustrative)
$$\Delta_r H^\circ \approx -4.0 \times 10^3 \text{ kJ kg}^{-1}$$

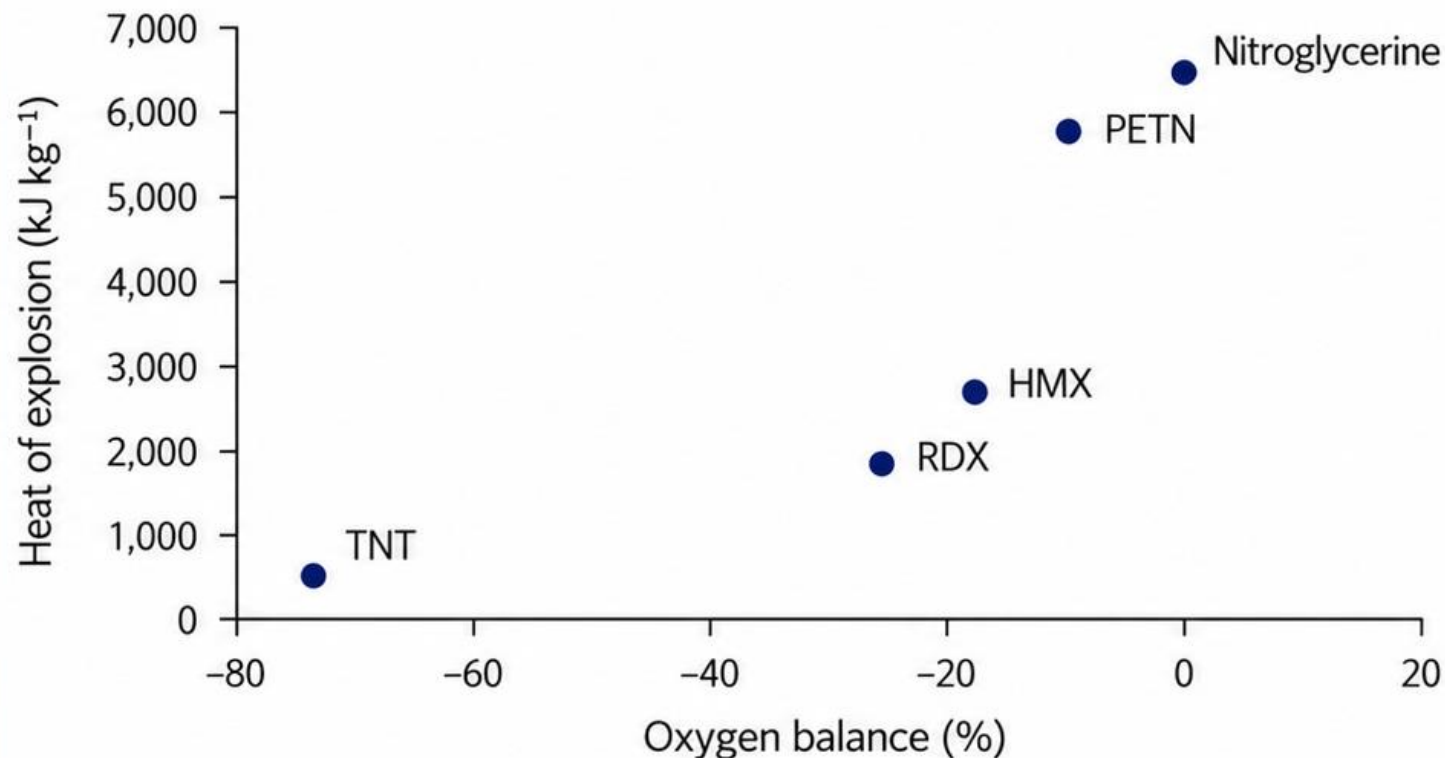
(value depends on assumed products and calculation method)

Key points:

- The heat of combustion is obtained from assumed products using formation enthalpies and Hess's law.
- The calculated value depends on the product set (more or less complete oxidation gives different values).
- These are approximate calculations; in practice the exact products and their amounts depend on temperature, pressure and equilibrium.

Does better oxygen balance mean more energy?

Experimental data for common energetic materials (Klapötke).



Key observations (Klapötke)

- Materials with oxygen balance closer to zero tend to have a greater heat of explosion.
- However, there is significant scatter and the relationship is not unique.

Important point

- Oxygen balance alone is insufficient for thermochemical prediction.
- Other factors, including molecular structure, bonding and the actual products formed, also influence the energy release.

Data from: Klapötke, T. M. *Explosives*, 3rd ed. (2017).

Is oxygen balance enough to rank energetic materials by energy release?

Activity 2: Does better oxygen balance always mean more energy?

Use the data from Klapötke (previous slide) to evaluate the following statement.

“The energetic material with oxygen balance closest to zero will always release the most energy.”

1

What overall trend can you see?

- Describe the general relationship between oxygen balance and heat of explosion.
- Is the trend linear?

2

Does the data support the word “always”?

- Are there any materials that do not follow the trend?
- What does this tell you about the statement?

3

Why might two materials with similar oxygen balance have different heats of explosion?

- Think about molecular structure, bonding and the actual products formed.
- Give specific examples from the data.

4

What other chemical information would you need for a better thermochemical prediction?

- Consider product distribution, bonding and molecular structure.
- What does oxygen balance not tell you?

Conclusion: Is oxygen balance a useful descriptor, a predictor, or both?



Activity 2: Suggested answers

Does better oxygen balance always mean more energy?

1

Overall trend

- As oxygen balance approaches zero, heat of explosion tends to increase.
- The trend is positive overall.
- The relationship is not perfectly linear.

2

Does the data support ‘always’?

- No.
- The plot shows scatter, so oxygen balance alone does not fully predict energy release.
- “Closest to zero” is a useful indicator, not an absolute rule.

3

Why can similar oxygen balances give different energies?

- Different molecular structures and bonding.
- Different assumed or actual reaction products.
- Thermochemical energy depends on more than oxygen availability.

4

What else is needed for a better prediction?

- Likely product distribution.
- Standard enthalpies of formation.
- Information about molecular structure and bonding.

Conclusion: Oxygen balance is a useful descriptor, but not a complete thermochemical predictor.

Oxygen balance: useful, but not sufficient

What oxygen balance tells us

- **Relative oxygen availability** in the composition
- Whether a material is **oxygen-deficient** or **oxygen-rich**
- A **broad** indication of likely oxidation **completeness** and the types of products that can form
- A useful way **to compare** different materials and formulations

What oxygen balance does not tell us

- The **exact product distribution** (e.g. CO_2 , CO , C , H_2O , N_2)
- The exact **enthalpy** or **internal energy** change (ΔH or ΔU)
- The **reaction rate** or decomposition mechanism
- The **sensitivity** or **stability**
- The **overall performance** as an energetic material

Oxygen balance is a descriptor of composition — not a complete predictor of energetic behaviour.

Next question: how is chemical energy converted into useful work?



Modern energetic materials: why oxygen balance is not enough

Same empirical elemental ratio → same oxygen balance

Does that mean the materials must behave identically?

No. Identical elemental ratios and oxygen balance do not imply identical molecular structure, physical properties, kinetics or sensitivity.

FOX-7

1,1-diamino-2,2-dinitroethylene (FOX-7)



- Empirical formula: CH₂N₂O₂
- Oxygen balance: 0 %
- Different molecular structure and bonding from RDX
- Lower sensitivity than RDX (in general)

Elemental composition

Element	FOX-7	RDX
C	2 (1)	3 (1)
H	4 (2)	6 (2)
N	4 (2)	6 (2)
O	4 (2)	6 (2)

Numbers in brackets show the empirical ratio.
Both have the empirical formula CH₂N₂O₂.



Different molecular structure

- Different arrangement of atoms and bonding
- Different intermolecular interactions and crystal structure
- Different physical properties (e.g. density, thermal stability)
- Different kinetics and sensitivity

RDX

1,3,5-trinitro-1,3,5-triazine (RDX)



- Empirical formula: CH₂N₂O₂
- Oxygen balance: 0 %
- Different molecular structure and bonding from FOX-7
- Higher sensitivity than FOX-7 (in general)



Key takeaway:

Oxygen balance is a compositional descriptor — not a complete predictor of energetic-material behaviour.

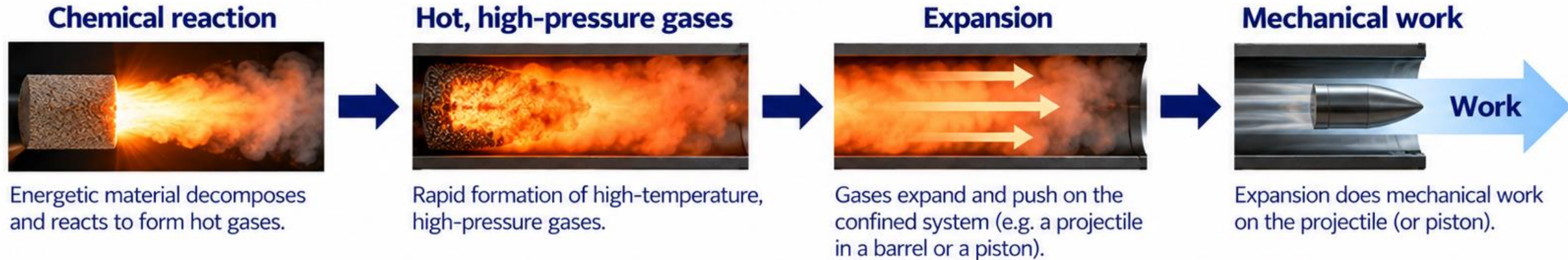
Part 5: From chemical energy to useful work

How is chemical energy delivered in a real OME system?



From chemical energy to useful work

The chemical energy released in an energetic material is converted into hot, high-pressure gases, which expand and can do mechanical work.



Thermochemistry

- Tells us how much chemical energy is released (e.g. ΔH , heat of explosion).
- Indicates the energy available in the gases.

System behaviour

- Determines how much of this energy is converted into useful work.
- Depends on gas expansion, pressure, volume change, and system design (e.g. barrel, chamber, piston).

Work done by a force

$$w = \int F dx$$

F = force (N)
 x = displacement (m)
 w = work (J)

For a projectile in a barrel

$$w = A \int p dx$$

A = cross-sectional area (m^2)
 p = pressure (Pa)
 x = projectile travel (m)
 w = work (J)

Energy available $\neq$ useful work delivered

How is propellant performance assessed in practice?

Propellant development (e.g. Thales) involves controlling the rate of gas generation, heat produced and maximum pressure, which are interdependent.

Formulation / composition



- Chemical composition and grain geometry.
- Controls energy content and surface area for burning.

Gas generation and heat release



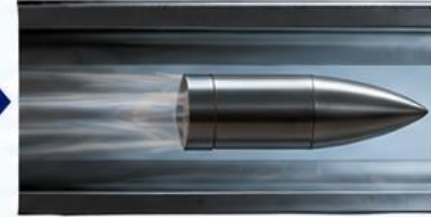
- Decomposition and combustion produce hot gases.
- Rate of gas generation and heat produced depend on formulation and burning rate.

Pressure development



- Hot gases increase the pressure in the confined system.
- The pressure profile depends on gas generation rate, heat release, grain design and chamber/barrel dimensions.

Projectile motion



- High-pressure gases push on the projectile.
- Projectile accelerates as it travels along the barrel.

Work delivered



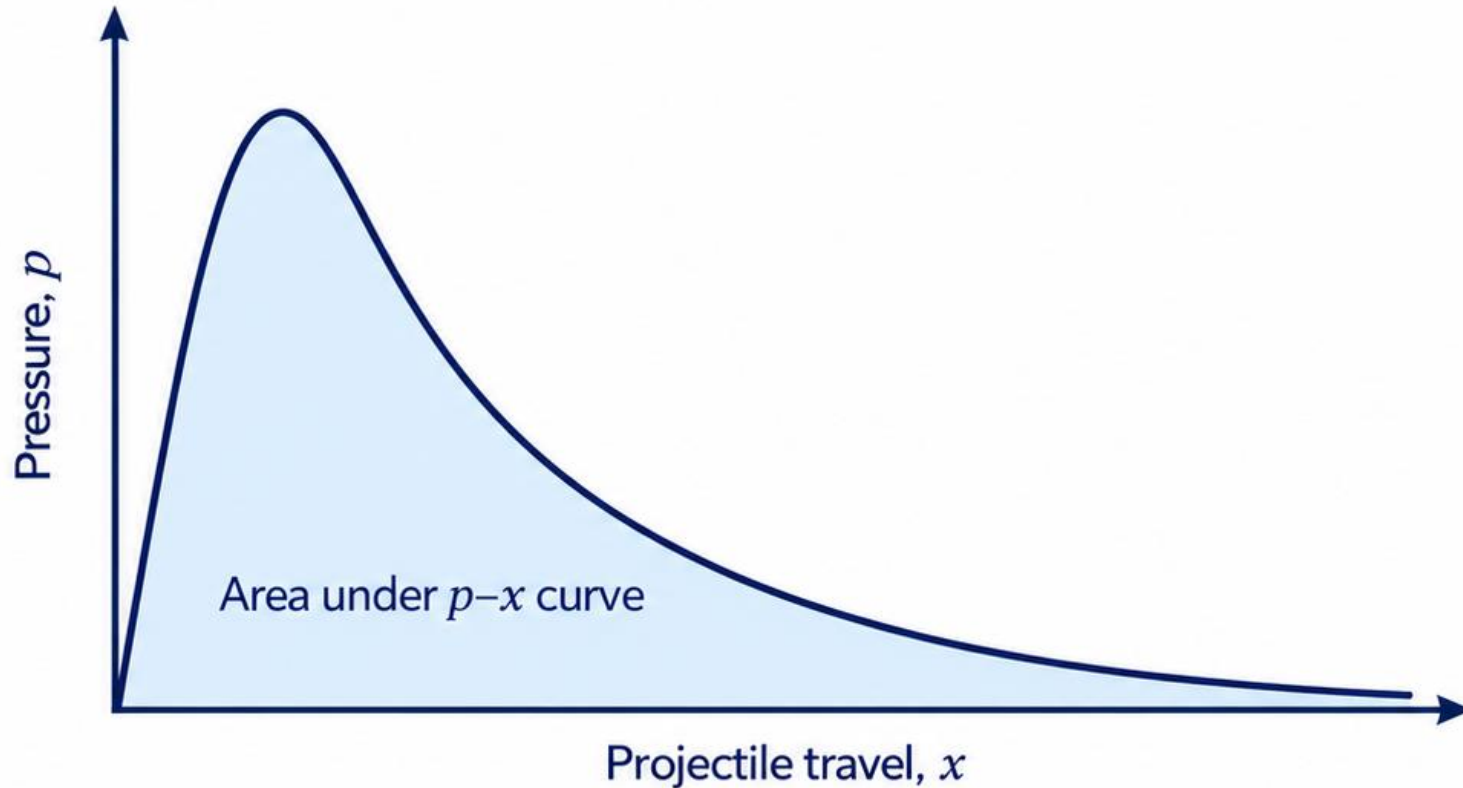
- Expansion of the gases does mechanical work on the projectile.
- Useful work depends on the pressure acting over the projectile travel distance.

The same chemical energy can be delivered differently depending on when and where pressure is generated.

To quantify the mechanical effect, Thales plots pressure against projectile travel.



Pressure–travel curves: where does the work come from?



$$W = A \int p \, dx$$

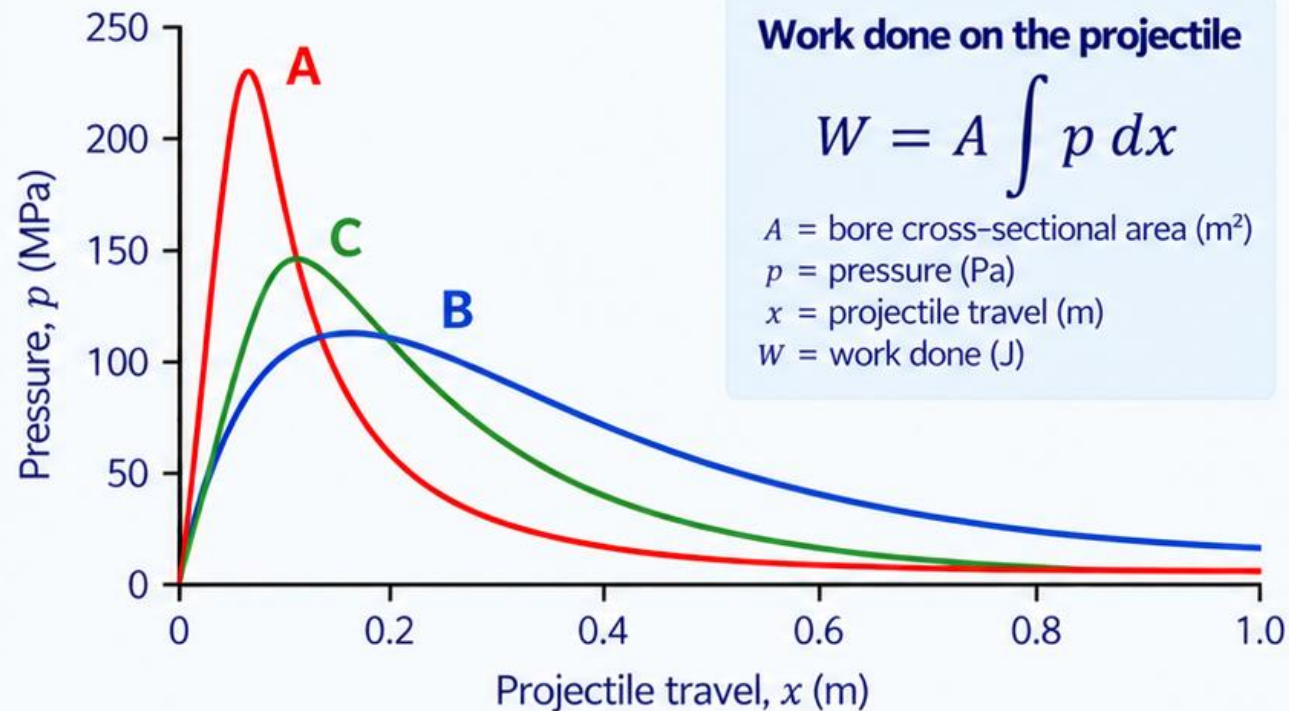
A = bore cross-sectional area

- Higher peak pressure does not necessarily mean more work
- Work depends on pressure acting over distance
- Area under the pressure–travel curve $\propto$ work done on the projectile

Peak pressure tells us the maximum load; area under the pressure–travel curve tells us about work delivered.

Activity 3: Peak pressure or useful work?

Consider the pressure–travel curves below for three different propellant formulations.



Questions

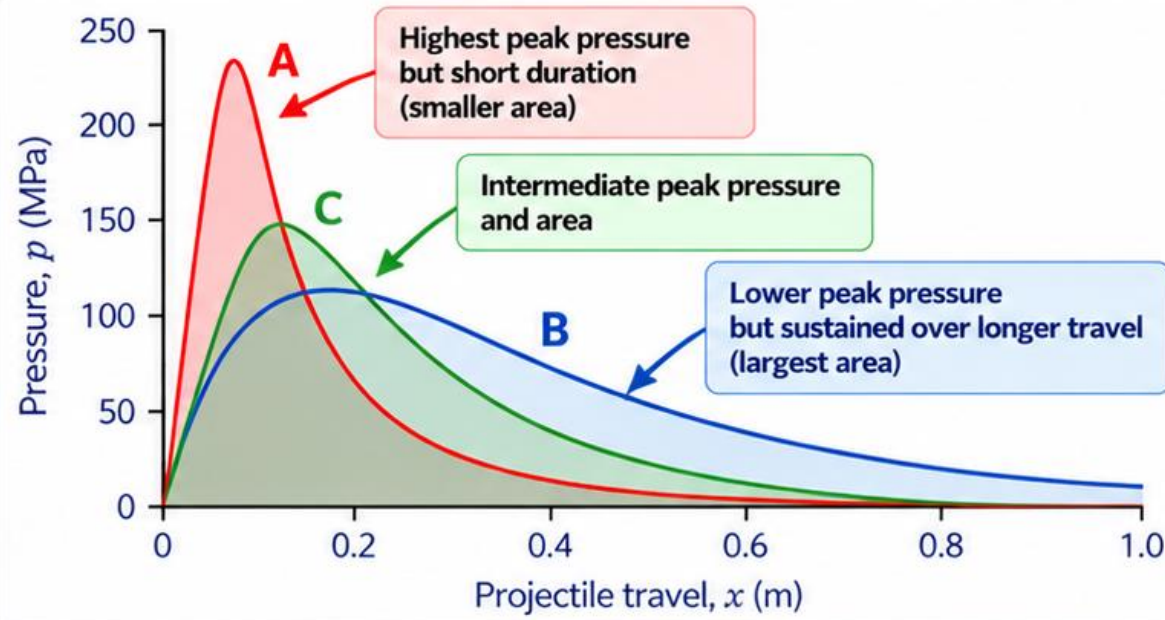
- 1 Which curve has the highest peak pressure?
- 2 Which curve appears to have the largest area under the pressure–travel curve?
- 3 Which formulation therefore delivers the most work to the projectile?
- 4 Does the highest peak pressure necessarily correspond to the greatest work? Explain.
- 5 Which aspects are mainly:
 - thermodynamic (related to chemical energy release)?
 - kinetic/system–design dependent (related to how the gases expand in the barrel)?

Useful work depends on how pressure is sustained over projectile travel, not just on the maximum pressure reached.



Activity 3: What determines useful work?

Analysis of the pressure–travel curves



Key points

- 1 Curve A has the highest peak pressure.
- 2 Curve B has the largest area under the pressure–travel curve and therefore delivers the most work to the projectile.
- 3 The highest peak pressure does not necessarily correspond to the greatest work.
- 4 Useful work depends on both the magnitude of the pressure and the distance over which it acts.

Curve	Peak pressure	Area under curve (relative work)	Interpretation
A	Highest	Smallest	High peak, rapid decay
C	Intermediate	Intermediate	Moderate peak and duration
B	Lowest	Largest	Lower peak, sustained pressure

Primarily thermodynamic factors

- Chemical energy available (e.g. ΔH , ΔU).
- Heat produced during reaction.
- Amount and type of gas that can be generated (oxygen balance, composition).
- Sets the potential amount of energy and gas available.

Primarily kinetic / system-design factors

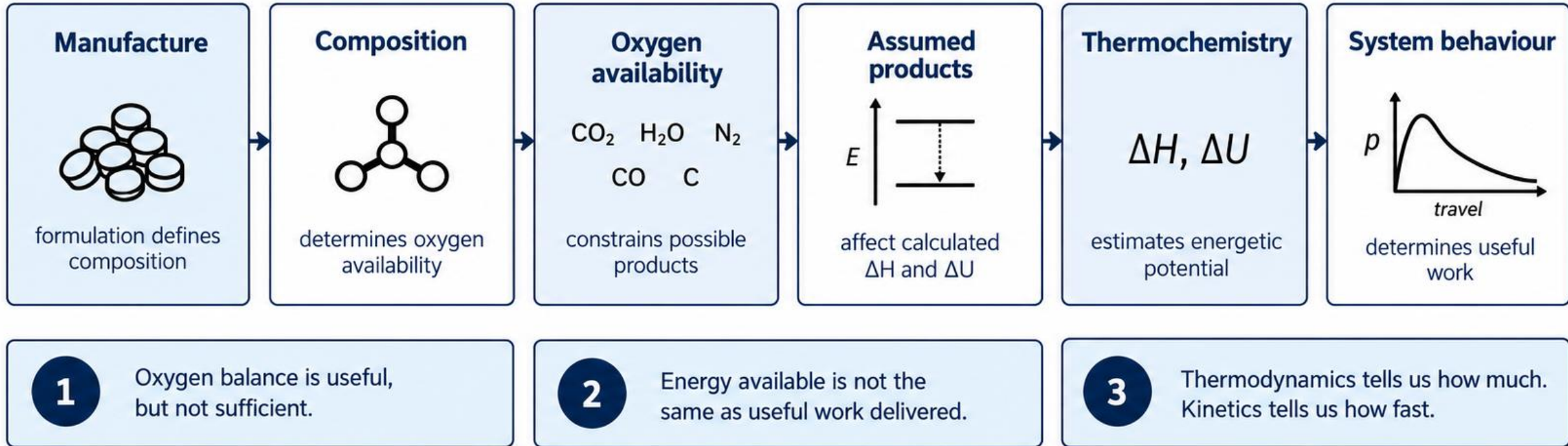
- Rate of gas generation (burning rate, decomposition kinetics).
- Pressure–time / pressure–travel profile.
- When the peak pressure occurs and how long pressure is sustained.
- Influenced by formulation, grain geometry and the system design (e.g. barrel, chamber).

**Thermochemistry determines the energetic potential;
kinetics and system design determine how that potential is delivered.**

Part 6: Session synthesis and link to S3

- Build the chemical argument for your presentation
 - **Turn your analysis** into a presentation argument
 - **From manufacture to use:** what have we established?
 - **Synthesis:** modern energetic-material design

From manufacture to use: what have we established?



S2: How much energy?

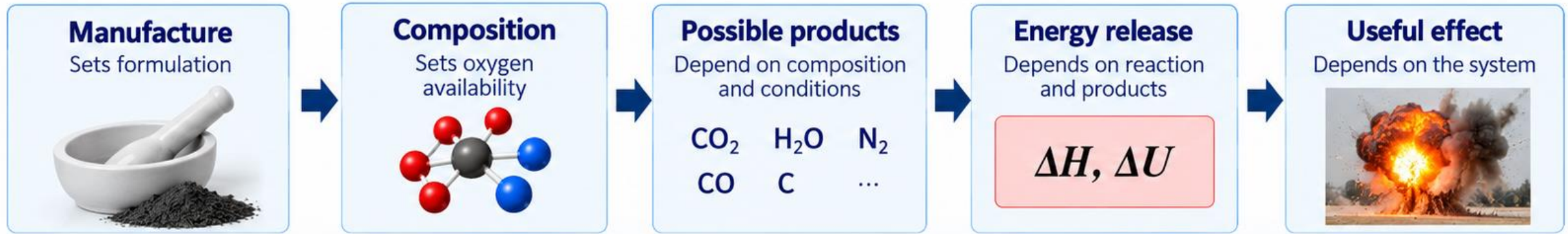
From formulation to energy release and useful work.



Next: Session 3

Chemical kinetics, decomposition and thermal stability.
How fast is the energy released?

Synthesis: modern energetic-material design



Modern design questions

Modern pyrotechnics

Can we retain the required heat and optical effect with less problematic chemistry?

- Alternative oxidisers
- Reduced heavy metals / smoke

Green propellants

Can we retain useful energy and gas generation while reducing lifecycle hazards?

- Reduced toxicity
- Compatibility and environmental impact

Modern explosives

Can we retain energetic potential while improving safety characteristics?

- Molecular structure matters
- Thermodynamics $\neq$ kinetics $\neq$ sensitivity



Modern energetic-material design is not simply about maximising energy.

It is about balancing energy, products, safety and application requirements.

Activity: Build the chemical argument for your presentation

Use the chemistry from today to build a clear chemical argument for your final presentation.

Group A – Modern Pyrotechnics

Can the required heat/light effect be retained while changing the formulation?



Consider changes to oxidiser, fuel or other components (e.g. reduced perchlorates or heavy metals).

Group B – Green Propellants

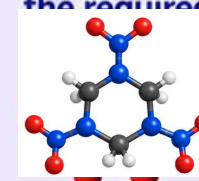
Can reduced-toxicity formulations retain useful energy and gas generation?



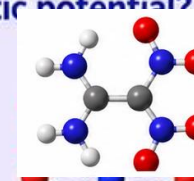
Consider alternative oxidisers (e.g. nitrates, dinitramides), fuel/binder choices and their impact on products, performance and environmental burden.

Group C – Modern Explosive Materials

Can changes in molecular structure or formulation improve safety while retaining the required energetic potential?



RDX



FOX-7

Consider how structure or formulation can influence oxygen availability, products, energy release and properties such as sensitivity.

Composition
(formulation/structure)



Oxygen availability
(oxygen balance)



Possible products
(depend on conditions)



Energy release
(ΔH , ΔU)



Application consequence
(useful effect)



Trade-off
(safety, environment, etc.)

Your task (15 minutes)

- 1 What changes chemically?**
Identify what could be changed in ingredient, formulation or molecular structure.
- 2 What thermochemical consequence could this have?**
Consider oxygen availability, likely products, and the effect on ΔH and/or ΔU .
- 3 What performance or functional requirement must be retained?**
For example: heat/light output, gas generation, energetic potential or useful work.
- 4 What trade-off must also be considered?**
Consider safety, sensitivity, toxicity, handling, compatibility or environmental impact.
- 5 What can you conclude – and what can you NOT conclude from thermochemistry alone?**
Be clear about what the evidence can and cannot tell you.



Time: 15 minutes

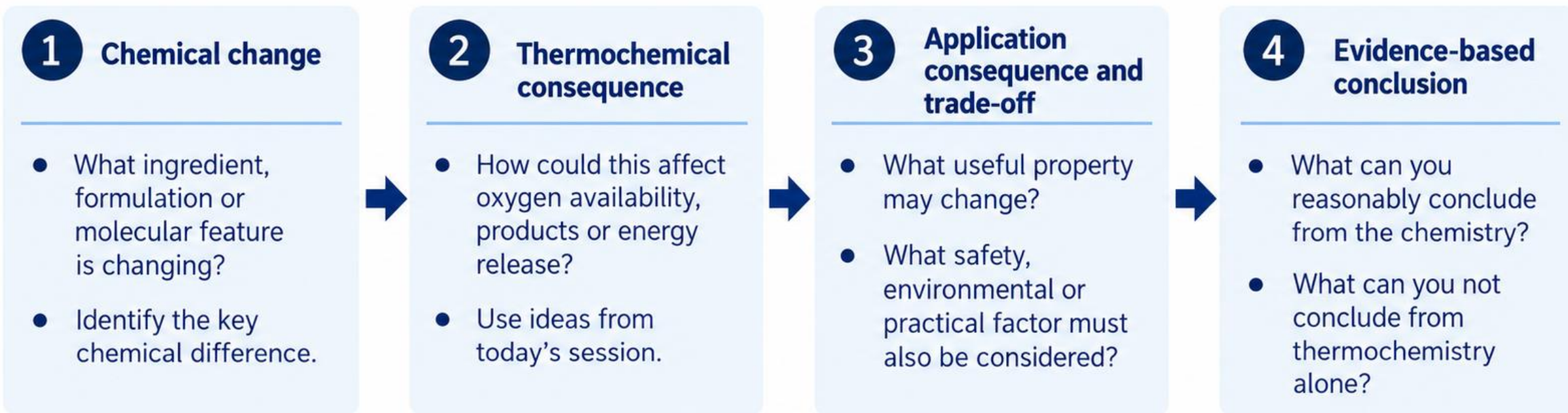
- Work in your group.
- Prepare one slide or one sheet summarising your analysis.
- Be ready to share a brief summary.

Finish with one evidence-based conclusion:

Changing _____ affects _____,
which leads to _____, but the trade-off is _____.

Turn your analysis into a presentation argument

Summarise your group's analysis as a clear, evidence-based argument.



Sentence template: Changing ____ affects ____, which may influence _____. However, _____ must also be considered.

One slide or one sheet per group