

Session 4

Thermodynamics, Equilibrium and Phase Behaviour

Lifecycle focus: Manufacture → Storage → Use



From Sessions 1–3 to Session 4

Building the chemistry across the OME lifecycle

Session 1

What have we made?

Reaction chemistry
of energetic materials



Session 2

How much chemical energy can it release?

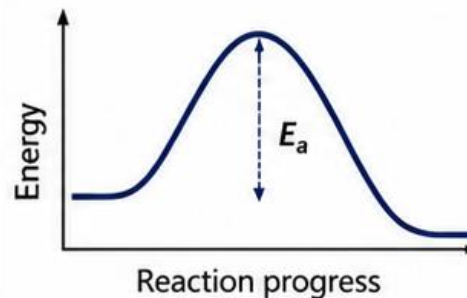
Thermochemistry
and composition



Session 3

How fast can it change or react?

Kinetics and decomposition
of energetic materials



Session 4

Which chemical or physical state is favoured?

Thermodynamics, equilibrium
and phase behaviour



Applying chemistry across the OME lifecycle

Central question
for this session:

Which chemical or physical state is favoured —
and why can a material sometimes remain in a different state?



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Session 4 roadmap

From thermodynamics to phase behaviour in OME

Part 1

What Drives Change?

- Enthalpy and entropy
- Gibbs energy
- Thermodynamics versus kinetics
- RDX storage stability



Part 2

Where Is Equilibrium?

- Explosive decomposition products
- Dynamic equilibrium
- Q and K
- Le Chatelier's principle
- Equilibrium predictions



Part 3

Phase Behaviour

- Gibbs energy and phase stability
- Chemical potential
- Crystallisation
- Nucleation and metastability
- Experimental evidence



Wrap-up

Connecting the Chemistry

- Thermodynamics, kinetics and evidence
- OME lifecycle implications
- Introduction to Session 5

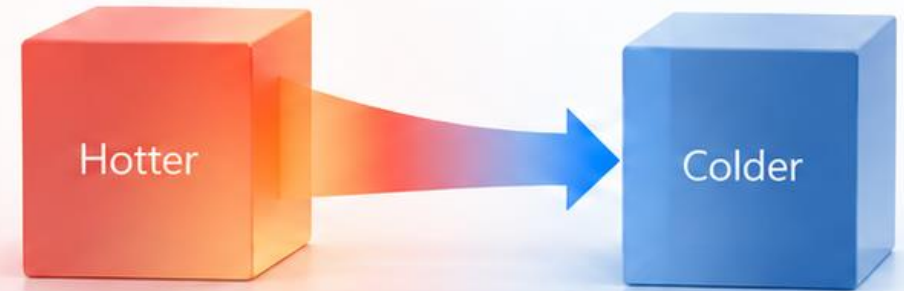
Part 1

What Drives Change?

Understanding why chemical and physical changes occur

Why do some changes occur spontaneously, while others do not?

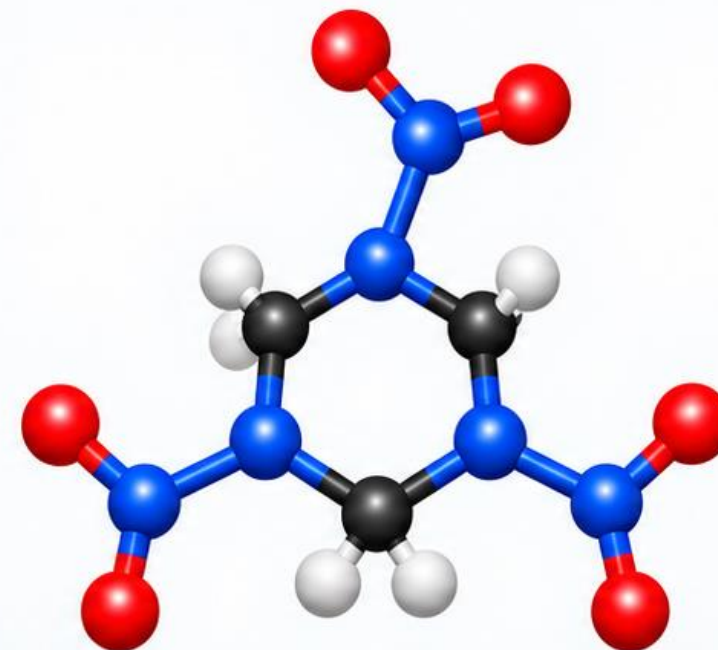
From energy conservation to entropy and Gibbs energy



Why Can Energetic Materials Remain Stable During Storage?

RDX (cyclotrimethylenetrinitramine)

- RDX can release substantial energy through exothermic decomposition reactions.
- Yet it can remain relatively unchanged for extended periods under suitable storage conditions.
- Understanding this behaviour is important when assessing chemical stability during manufacture and storage.



QUESTION

Does the ability to release a large amount of energy mean that a material must decompose rapidly?

Why Is Heat Release Not Enough?

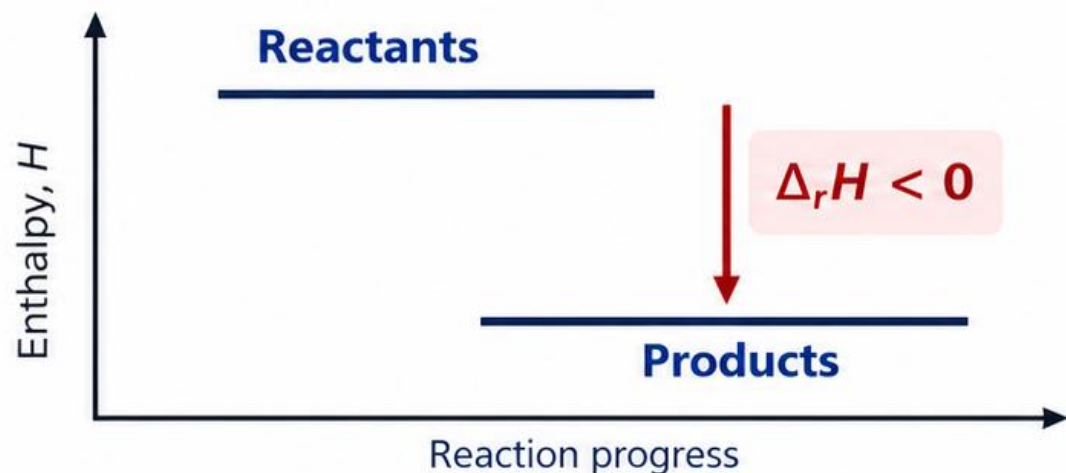
Energy conservation and reaction enthalpy do not, on their own, predict spontaneous change.

OME EXAMPLE

Hydrogen peroxide decomposition in propulsion



What the enthalpy diagram shows



What the chemistry tells us

1 First Law of thermodynamics

$$\Delta U = q + w$$

Energy is conserved in either direction
(w = work done on the system).

2 Reaction enthalpy

$$\Delta_r H = \Delta_r H(\text{products}) - \Delta_r H(\text{reactants})$$

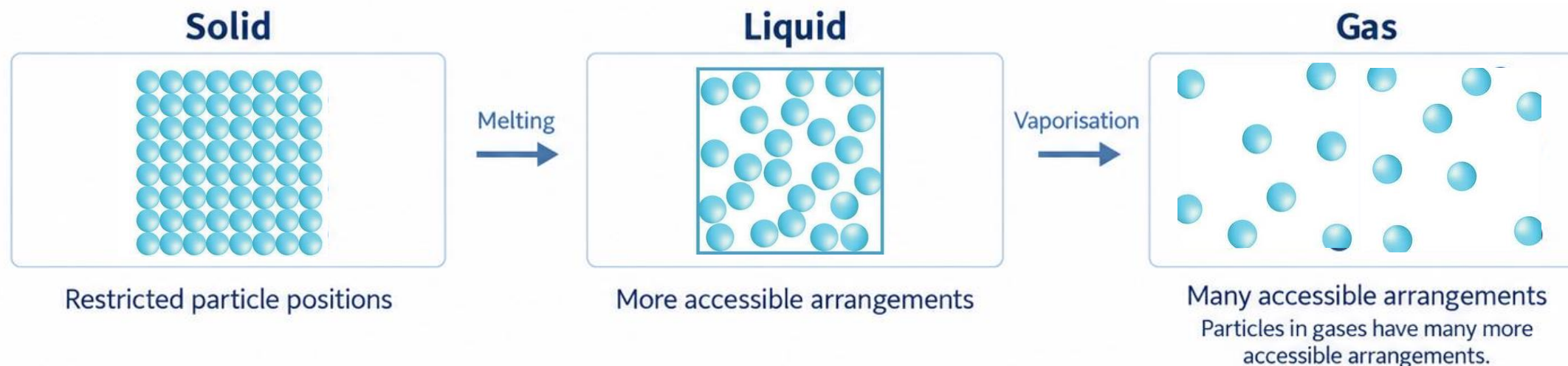
$\Delta_r H < 0$: heat released at constant pressure
(when only pressure–volume work is involved).



Enthalpy alone cannot determine thermodynamic favourability — entropy and temperature also matter. Reaction speed depends on kinetics.

What Is Entropy?

Entropy is a thermodynamic property related to the number of accessible microscopic states.



$$S_m(\text{solid}) < S_m(\text{liquid}) < S_m(\text{gas})$$

For the same substance, melting and vaporisation increase entropy at their transition conditions.

Entropy, S

Units: J K^{-1}

Molar entropy, S_m

Units: $\text{J mol}^{-1} \text{K}^{-1}$

Key takeaway: Entropy depends on temperature, physical state, and the nature and amount of substance.

Entropy Changes During Energetic Decomposition Reactions

Example: decomposition reaction that forms a gaseous product.



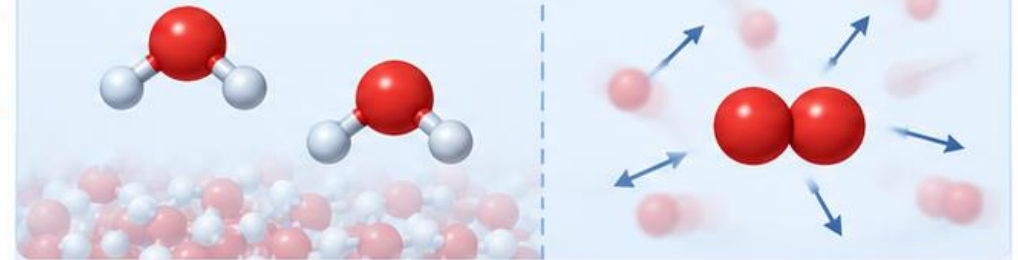
Reactant: hydrogen peroxide (liquid)



Molecules in a liquid have relatively restricted movement and arrangements.

Decomposition

Products: water (liquid) and oxygen (gas)



Water remains a liquid with similar restrictions.

Oxygen is a gas with many accessible microscopic states (translational, rotational and vibrational).

- Chemical reactions can change entropy because the **number, type** and **physical state** of particles can change.
- Formation of gaseous products often increases entropy because gases have **many accessible microscopic states**.

Standard reaction entropy:

$$\Delta_r S^\circ = \sum_{\text{products}} \nu_i S^\circ - \sum_{\text{reactants}} \nu_i S^\circ$$



OME link: formation of gaseous products matters because it can influence pressure generation, expansion and energetic-material behaviour.



The Second Law: System and Surroundings

A spontaneous change increases the total entropy of the universe (system + surroundings).

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

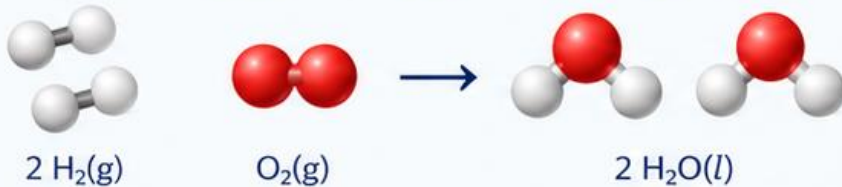
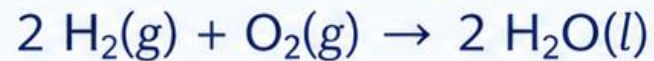
Spontaneous (irreversible) change: $\Delta S_{\text{universe}} > 0$

At equilibrium: $\Delta S_{\text{universe}} = 0$

Reversible change: $\Delta S_{\text{universe}} = 0$

Example: formation of liquid water from hydrogen and oxygen

System: reacting gases



$$\Delta S_{\text{system}} < 0$$

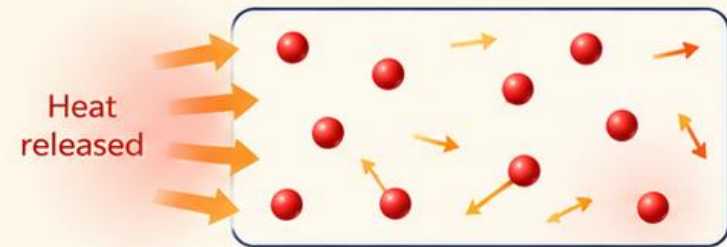
Fewer accessible molecular arrangements in the products (gases → liquid).

Heat released to surroundings (exothermic reaction)



Energy is transferred as heat, increasing the entropy of the surroundings.

Surroundings: the environment



$$\Delta S_{\text{surroundings}} > 0$$

The transferred heat increases the number of accessible microstates in the surroundings.

Question:

Can a spontaneous change occur even if the entropy of the system decreases?

From the Second Law to Gibbs Energy

Why do we use Gibbs energy to predict chemical change?

The Second Law

Spontaneous change increases the total entropy of the system and surroundings.

A practical criterion

At constant temperature and pressure, the system's properties can tell us which changes are thermodynamically favoured.

GIBBS ENERGY CHANGE

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G < 0$ Thermodynamically favoured at constant T and p

OME link: A thermodynamically favoured decomposition pathway may proceed very slowly because of kinetic barriers.

Gibbs Energy: What Does Its Sign Tell Us?

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

At constant temperature and pressure, the reaction Gibbs energy indicates which direction of a reaction is thermodynamically favoured.

Interpreting the sign of $\Delta_r G$

$$\Delta_r G < 0$$

Forward reaction is thermodynamically favoured.

$$\Delta_r G = 0$$

Reaction is at equilibrium.

$$\Delta_r G > 0$$

Reverse reaction is thermodynamically favoured.

Example: decomposition of hydrogen peroxide



$\text{H}_2\text{O}_2 (l)$



$\text{H}_2\text{O} (l)$

+



$\text{O}_2 (g)$

$$\Delta_r H^\circ < 0$$

Exothermic reaction — heat is released.

$$\Delta_r S^\circ > 0$$

Formation of gaseous oxygen contributes to an increase in entropy.

$$\Delta_r G^\circ < 0$$

The forward reaction is thermodynamically favoured under standard-state conditions.

Question: Can an endothermic reaction ($\Delta_r H > 0$) still be thermodynamically favoured?

Can Temperature Change the Favoured Direction?

Gibbs energy combines enthalpy and entropy to assess thermodynamic favourability.

$$\Delta G = \Delta H - T\Delta S$$

Changing temperature changes $T\Delta S$, even when ΔH and ΔS are approximately constant.

PROCESS A · HYPOTHETICAL

$$\Delta H = -25 \text{ kJ mol}^{-1}$$

$$\Delta S = -50 \text{ J mol}^{-1} \text{ K}^{-1}$$

Calculate ΔG at 298 K.

1. Convert ΔS to $\text{kJ mol}^{-1} \text{ K}^{-1}$.
2. Identify the favoured direction.

PROCESS B · HYPOTHETICAL

$$\Delta H = +12 \text{ kJ mol}^{-1}$$

$$\Delta S = +50 \text{ J mol}^{-1} \text{ K}^{-1}$$

Calculate ΔG at 298 K and 200 K.

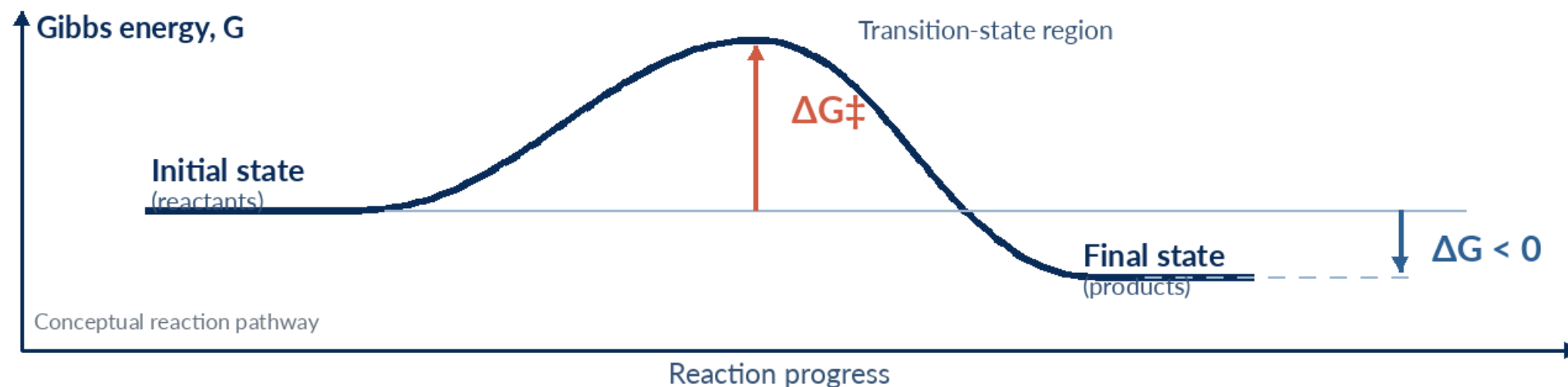
1. Convert ΔS to $\text{kJ mol}^{-1} \text{ K}^{-1}$.
2. Compare the favoured direction.

DISCUSS Can temperature reverse the thermodynamically favoured direction? Explain.

OME LINK Temperature affects thermodynamics and reaction kinetics through different relationships.

Thermodynamically Favoured Does Not Mean Fast

A negative Gibbs energy change indicates favourability, not how quickly a change occurs.



Thermodynamics

Determines whether the forward change is favoured ($\Delta G < 0$).

Kinetics

Activation barriers influence how quickly it occurs ($\Delta G^\ddagger$).

OME connection An energetic material may have thermodynamically favoured decomposition pathways yet remain relatively unchanged during storage because they are kinetically hindered.

Question If decomposition is thermodynamically favoured, why might an energetic material remain unchanged during storage?

Applying Thermodynamics to OME Storage Stability

An energetic material's potential to release energy does not, by itself, determine its storage stability. We need to consider thermodynamics, kinetics and experimental evidence.

Thermodynamics

Is decomposition thermodynamically favoured?

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G < 0$$

indicates the decomposition reaction is thermodynamically favoured under the conditions considered.

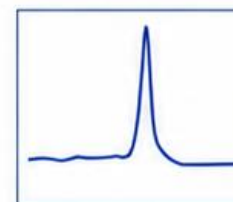
Kinetics

How rapidly could decomposition proceed?

- Activation barriers and reaction mechanisms control the rate.
- A thermodynamically favoured reaction can still be very slow if the activation barrier is high.
- Temperature influences the rate of decomposition.

Experimental evidence

Is chemical change actually detected during storage or testing?



DSC

Heat-flow changes during a controlled temperature programme. Identifies thermal events.



HFC

Detects very small heat releases associated with slow decomposition or ageing.



HPLC

Identifies changes in chemical composition. Detects parent compounds and degradation products (where suitable methods are available).

Storage stability cannot be determined from reaction energetics alone.

A complete assessment combines thermodynamics (ΔG), kinetics (rate) and experimental evidence.

Question:

If RDX shows no measurable decomposition during a laboratory experiment, can we conclude that it will remain stable indefinitely?



Summary: What Drives Change?

OUR OPENING QUESTION

Why can RDX remain relatively unchanged during storage despite its energetic character?

01

THERMODYNAMICS

Gibbs energy determines whether a specified change is favoured.

02

KINETICS

Activation barriers influence how rapidly the change occurs.

03

EXPERIMENTAL EVIDENCE

Measurements establish what changes occur under the tested conditions.

ANSWER TO THE RDX QUESTION

RDX may have thermodynamically favoured decomposition pathways, but kinetic barriers can make chemical change very slow under suitable storage conditions.



Part 2

Where Is Equilibrium?

Understanding how reacting systems reach a thermodynamic balance.



If thermodynamics determines the favoured direction, what happens when there is no further driving force?

Why Does Chemical Equilibrium Matter in OME?

Explosive decomposition does not necessarily produce one fixed mixture of products.

1 Elemental composition

Oxygen balance constrains possible product mixtures, but cannot determine their precise proportions.

2 Reactions between products

Decomposition products may react further and interconvert through reversible reactions.

3 Why composition matters

Product proportions influence reaction energetics and the properties of the resulting gases.

Akhavan example: a reversible reaction among gaseous decomposition products



Temperature and mixture composition influence the thermodynamically favoured direction.

QUESTION

Can one balanced equation predict every decomposition product?

What Is Chemical Equilibrium?

Reversible reactions among explosive decomposition products

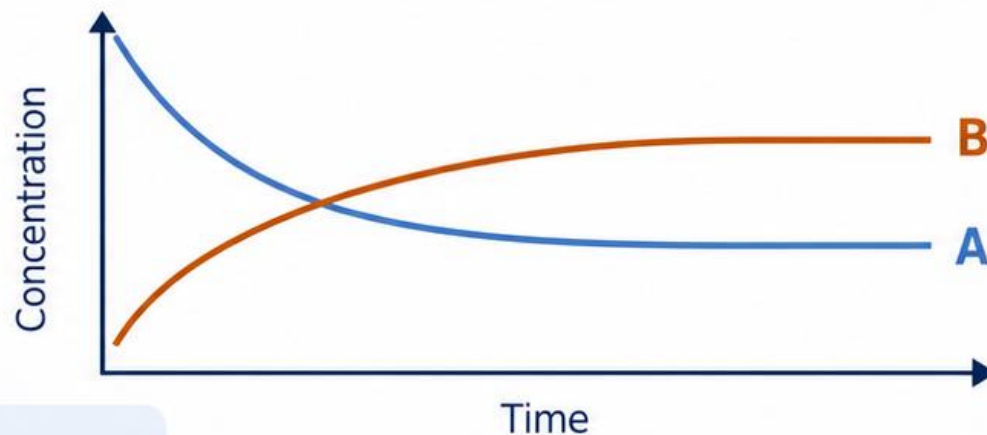
Example from decomposition-product chemistry



At equilibrium

- **Forward rate = reverse rate**
- Concentrations remain constant with time
- **Concentrations need not be equal**

Concentration versus time



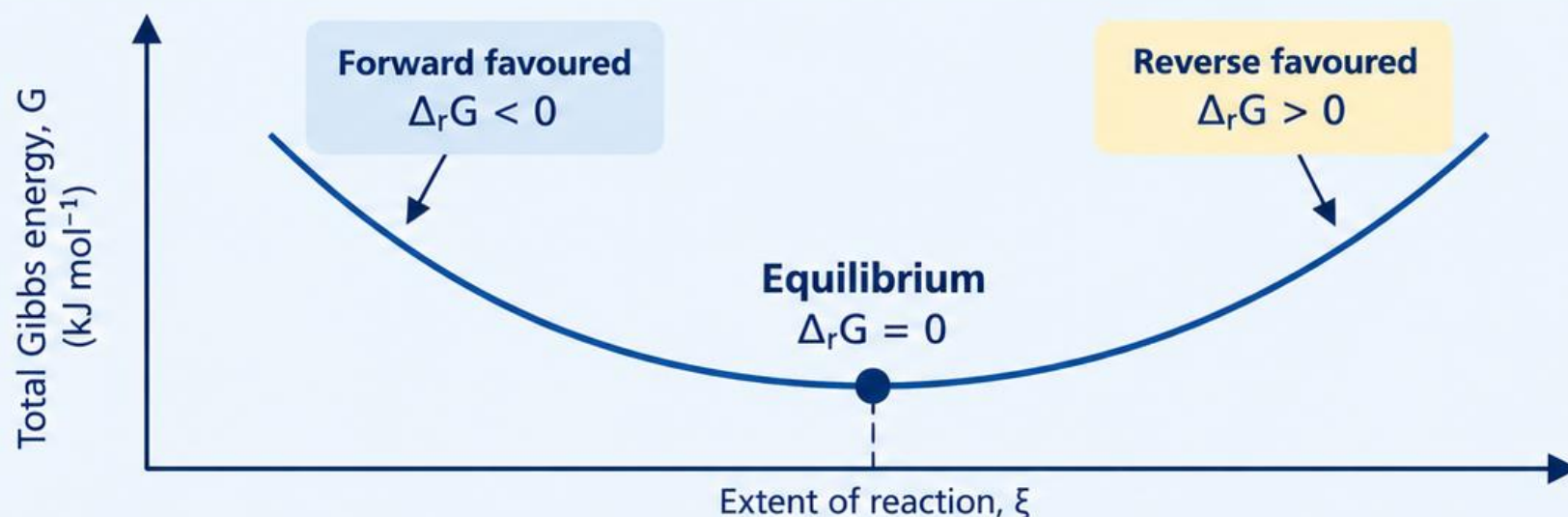
Ask students: Do equal rates mean equal concentrations?

OME link: decomposition products can interconvert while their equilibrium proportions stay constant.

How Does Gibbs Energy Explain Equilibrium?

At constant temperature and pressure, equilibrium corresponds to a minimum in total Gibbs energy.

Example: equilibrium among explosive decomposition products



The slope of the curve corresponds to the reaction Gibbs energy:

- Left: forward change lowers G ($\Delta_r G < 0$).
- Right: reverse change lowers G ($\Delta_r G > 0$).
- At equilibrium: $\Delta_r G = 0$ and total G is at a minimum (not necessarily zero).

At equilibrium, the reaction Gibbs energy is zero, but the total Gibbs energy is at a minimum — not necessarily zero.

OME link:

Equilibrium predicts the relative proportions of CO_2 , CO , H_2 and H_2O among explosive reaction products, under specified conditions, provided the reacting mixture can reach equilibrium.



The Reaction Quotient and the Equilibrium Constant

Q describes the current mixture; K is the value of Q at equilibrium.



$$Q = \frac{(p_{\text{CO}}/p^\circ)(p_{\text{H}_2\text{O}}/p^\circ)}{(p_{\text{CO}_2}/p^\circ)(p_{\text{H}_2}/p^\circ)}$$

$$K = \frac{(p_{\text{CO,eq}}/p^\circ)(p_{\text{H}_2\text{O,eq}}/p^\circ)}{(p_{\text{CO}_2,\text{eq}}/p^\circ)(p_{\text{H}_2,\text{eq}}/p^\circ)}$$

At equilibrium: $Q = K$

Q : composition at any moment

K : equilibrium value
at a given temperature

For ideal gases, *partial pressures* may be used.

products $\rightarrow$ numerator

reactants $\rightarrow$ denominator

stoichiometric coefficients $\rightarrow$ exponents

$$K \gg 1$$

products strongly favoured

$$K \approx 1$$

neither side strongly favoured

$$K \ll 1$$

reactants strongly favoured

Question: If we calculate Q , how do we know whether the mixture is at equilibrium?



How Can We Predict Reaction Direction?

The sign of $\Delta_r G$ depends on the ratio of the current composition to the equilibrium composition.

$$\Delta_r G = RT \ln \left(\frac{Q}{K} \right)$$

Where:

$\Delta_r G$: reaction Gibbs energy at the current composition (J mol^{-1})
 R : $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
 T : temperature (K)
 Q : reaction quotient
 K : equilibrium constant (at a given T)

Predicting reaction direction

Comparison	Value of $\Delta_r G$	Result
$Q < K$	$\Delta_r G < 0$	Forward reaction favoured (towards products)
$Q = K$	$\Delta_r G = 0$	System at equilibrium (no net change)
$Q > K$	$\Delta_r G > 0$	Reverse reaction favoured (towards reactants)

Example: decomposition product equilibrium



At a given temperature (hypothetical values):

$$Q = 0.10 \quad K = 0.40$$

Since $Q < K$, $\Delta_r G < 0$ and the forward reaction is thermodynamically favoured (towards CO and H_2O).

Key takeaway:

To predict the direction of change, compare Q with K . K alone does not tell us the direction of change for the current mixture.

Important:

Thermodynamic favourability does not tell us how fast equilibrium is reached (that depends on kinetics).



Activity: Predicting Reaction Direction

Equilibrium among gaseous decomposition products



A gas mixture at a specified temperature has the following partial pressures:

Species	CO ₂	H ₂	CO	H ₂ O
Partial pressure, p / bar	0.20	0.50	1.00	0.40

Equilibrium constant at this temperature (hypothetical value): **$K = 1.50$**

Tasks

1. Calculate the reaction quotient, Q , for this mixture.
2. Compare Q with the equilibrium constant, K .
3. Identify the thermodynamically favoured reaction direction.
4. Predict which gaseous species will increase and decrease as the mixture approaches equilibrium.



Possible Answers: Which Direction Is Thermodynamically Favoured?

Equilibrium among explosive decomposition products



A gas mixture at a specified temperature has these partial pressures:

Species	CO ₂	H ₂	CO	H ₂ O
p / bar	0.20	0.50	1.00	0.40

Equilibrium constant at this temperature: **K = 1.50**

1. Calculate the reaction quotient, Q

$$Q = \frac{p_{\text{CO}} \times p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} \times p_{\text{H}_2}}$$

$$Q = \frac{1.00 \times 0.40}{0.20 \times 0.50}$$

$$Q = \mathbf{4.00}$$

2. Compare with the equilibrium constant

Q = 4.00 and K = 1.50,
therefore Q > K.

3. Conclusion

The reverse reaction is thermodynamically favoured.

4. Composition change

- The current mixture contains too much CO and H₂O relative to equilibrium.
- CO and H₂O will be consumed.
- CO₂ and H₂ will be formed.
- The system will move left until Q = K.

Thermodynamically favoured direction **does not** tell us how fast equilibrium is reached.

Le Chatelier's Principle: How Does Equilibrium Respond to Change?

When a system at equilibrium is disturbed, its composition changes in a direction that tends to oppose the imposed disturbance.



Forward reaction is endothermic $\Delta_r H^\circ > 0$

Change	Equilibrium response	Why?
Increase temperature	Favours CO and H ₂ O	Forward reaction is endothermic
Decrease temperature	Favours CO ₂ and H ₂	Reverse reaction is exothermic
Increase pressure (ideal gases)	No shift	Two moles of gas on each side
Add CO ₂	Favours CO and H ₂ O	Composition change makes the forward direction favoured

Key idea: temperature changes K; pressure and composition can change Q.

Question: Why does compression not shift this equilibrium for ideal gases?



Equilibria Among Explosive Decomposition Products

Different equilibria respond differently to changes in temperature, pressure and composition.

Equilibrium 1: Gas–gas reaction



Forward reaction is endothermic ($\Delta_r H^\circ > 0$)

Change	Equilibrium response	Why?
Increase temperature	Favours CO and H ₂ O	Endothermic direction favoured
Add CO ₂	Favours CO and H ₂ O	Increases reactant concentration (Q decreases)
Increase pressure (ideal gases)	No shift	Two moles of gas on each side ($\Delta n_{\text{gas}} = 0$)

Consequence: At higher temperature, a greater proportion of CO may be present in the gaseous decomposition products.

Equilibrium 2: Formation of solid carbon (Boudouard reaction)



Forward reaction is exothermic ($\Delta_r H^\circ < 0$)

Change	Equilibrium response	Why?
Increase pressure	Favours C and CO ₂	Fewer moles of gas on product side (2 → 1)
Increase temperature	Favours CO	Forward reaction is exothermic, so heating favours the reverse direction
Add CO	Favours C and CO ₂	Increases reactant concentration (Q decreases)

Consequence: Solid carbon (C) may become thermodynamically favoured under some conditions, such as higher pressure or lower temperature.

Key point: Changing temperature, pressure or composition can alter the predicted composition of explosive decomposition products. However, the actual products observed also depend on reaction kinetics and may not reach equilibrium.



Why Might Actual Products Differ from Equilibrium Predictions?



Reaction kinetics

Insufficient time to reach equilibrium



Changing conditions

Rapid expansion and cooling



Experimental evidence

Measured composition and uncertainty

Key message: Equilibrium calculations provide useful predictions, but actual explosive decomposition products depend on both thermodynamics and kinetics.



Summary: What Determines Explosive Decomposition Products?

1. Elemental composition and oxygen balance

Determine which products are possible, but do not uniquely fix the final composition.

2. Chemical equilibrium

Gibbs energy determines the favoured direction; Q and K indicate whether a mixture is at equilibrium.

3. Conditions

Temperature, pressure and composition can shift the product distribution.

4. Reaction kinetics

Rapid reaction, expansion and cooling may prevent the equilibrium composition from being achieved.



Example discussed by Akhavan.

Can we predict the products of an explosive reaction from its molecular formula alone?

No — we must also consider equilibrium, conditions and kinetics.

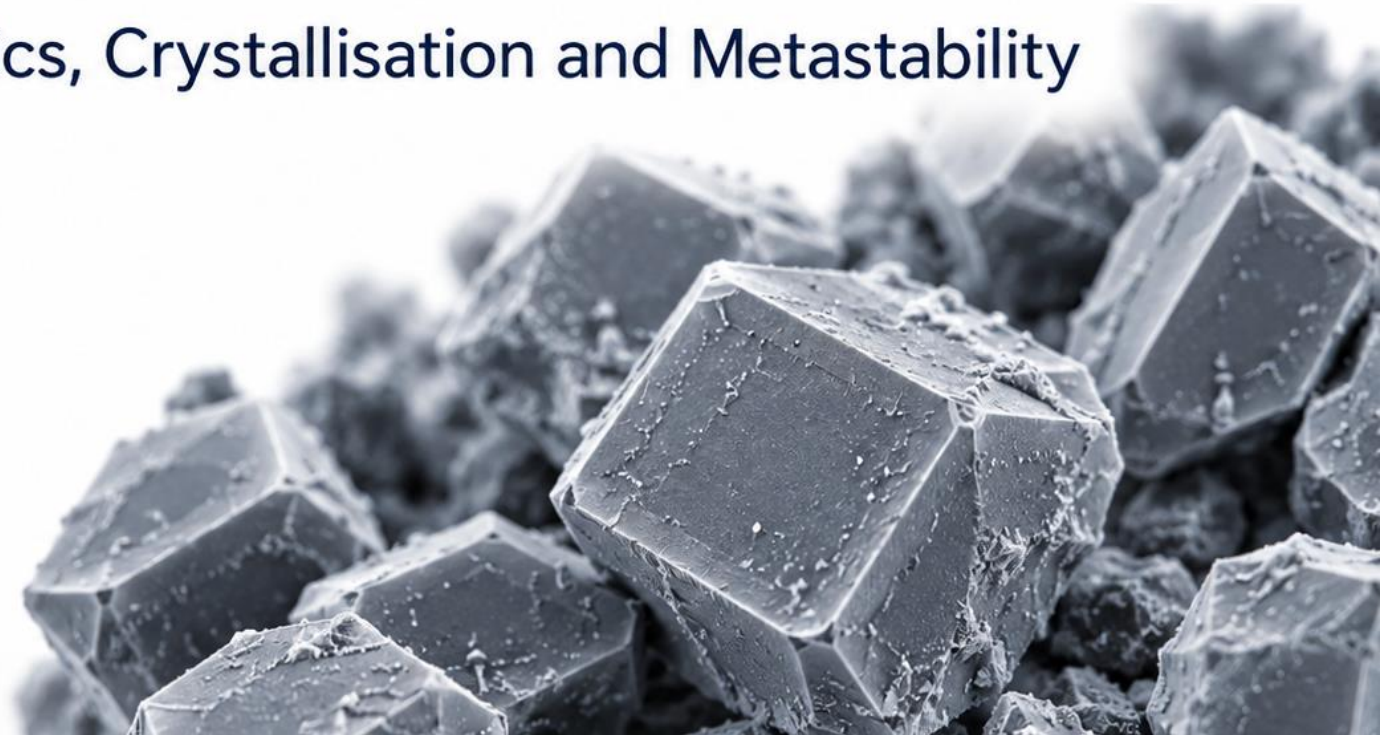
Answer: The products of explosive decomposition are governed by composition and thermodynamics, but the products actually observed also depend on kinetics and the reaction conditions.



Part 3

Phase Behaviour of Energetic Materials

Thermodynamics, Crystallisation and Metastability



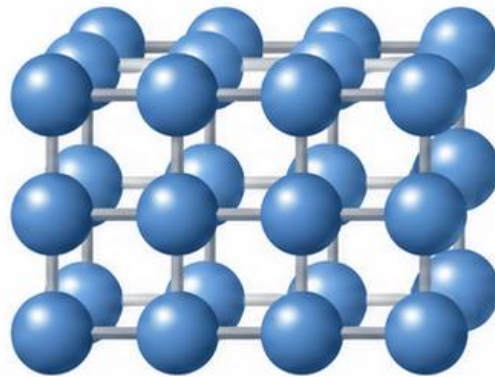
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Enthalpy and Entropy in Phase Transitions

Competing enthalpy and entropy contributions determine the thermodynamic driving force for phase changes.

$$\Delta G = \Delta H - T\Delta S$$



Solid

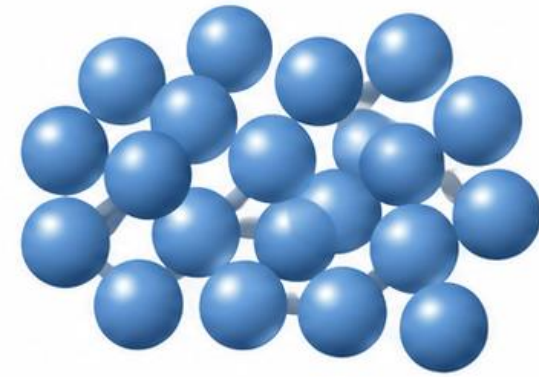
Ordered arrangement
of particles

Melting



$$\Delta H > 0$$

$$\Delta S > 0$$

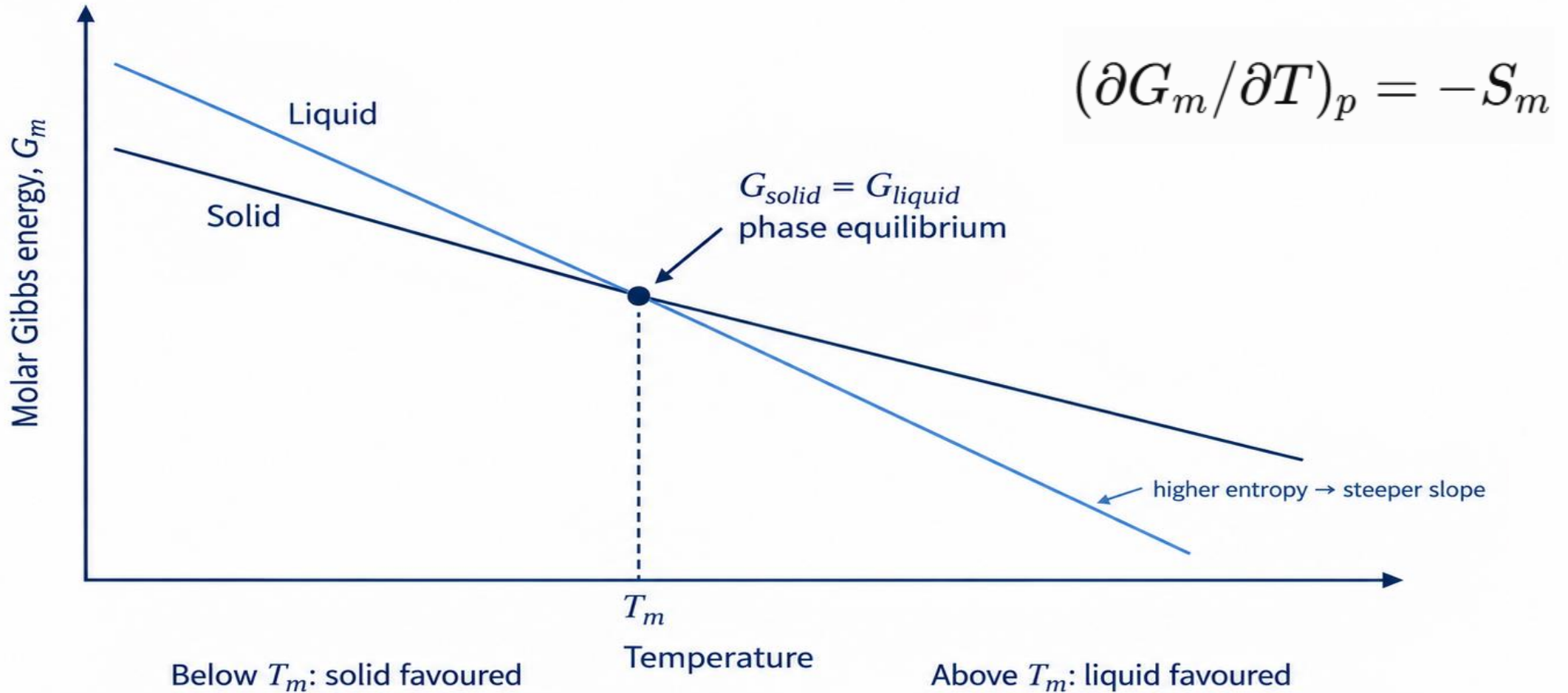


Liquid

Close together but
disordered

Gibbs Energy Determines Phase Stability

At a specified temperature and pressure, the phase with the lowest molar Gibbs energy is thermodynamically favoured.



When Are Two Phases in Equilibrium?

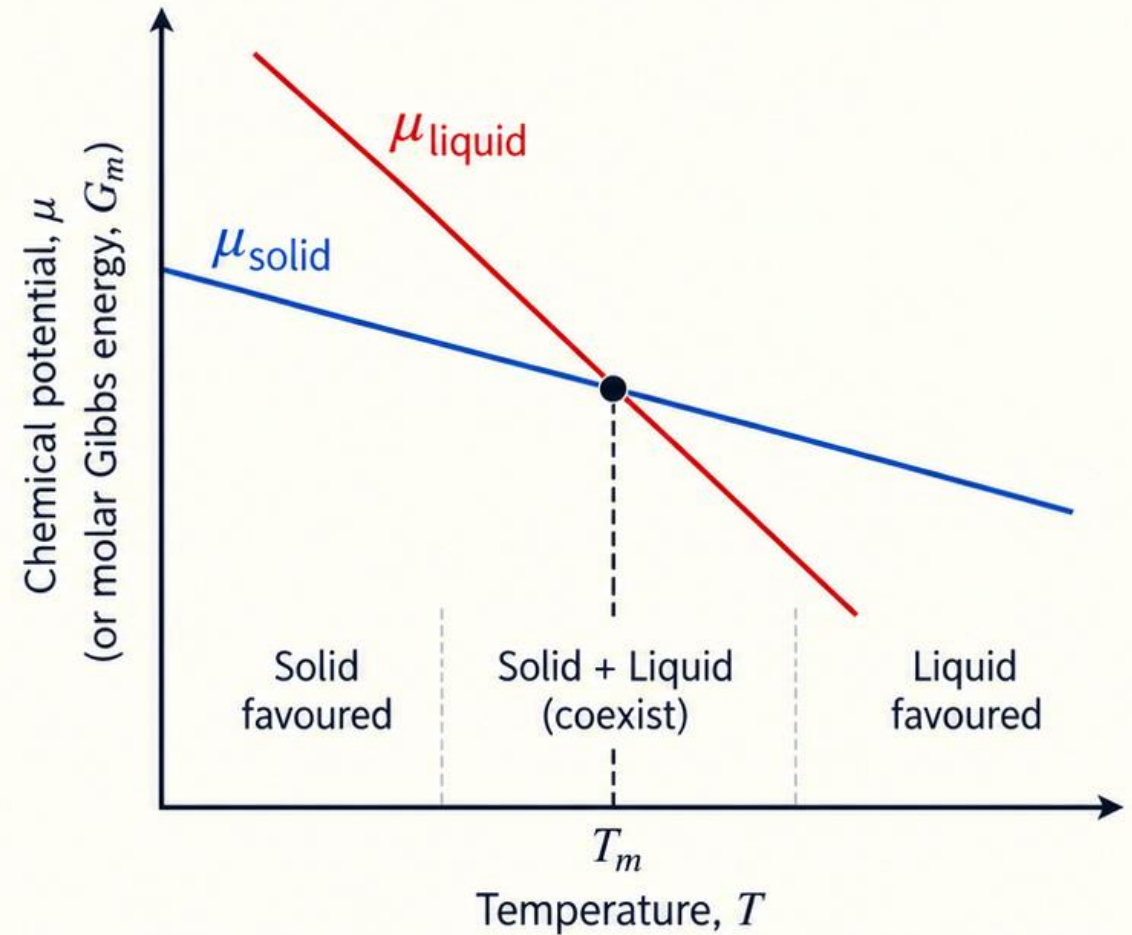
Coexisting equilibrium phases have equal chemical potentials.

Chemical potential (μ) is the partial molar Gibbs energy of a substance. For a pure phase, $\mu = G_m$.

At solid-liquid equilibrium:

$$\mu_{\text{solid}} = \mu_{\text{liquid}}$$

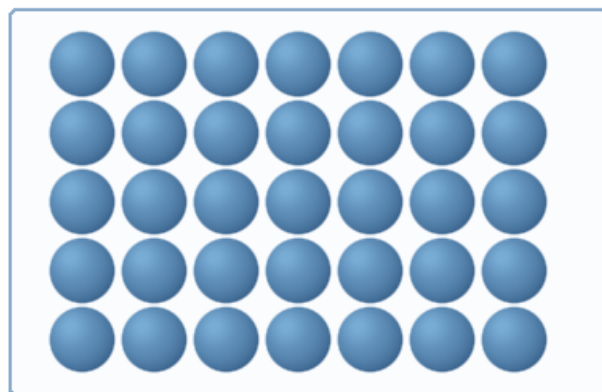
- $T < T_m$: $\mu_{\text{solid}} < \mu_{\text{liquid}}$ (solid is favoured)
- $T = T_m$: $\mu_{\text{solid}} = \mu_{\text{liquid}}$ (phases coexist)
- $T > T_m$: $\mu_{\text{solid}} > \mu_{\text{liquid}}$ (liquid is favoured)



When Are Two Phases in Equilibrium?

Coexisting equilibrium phases have equal chemical potentials.

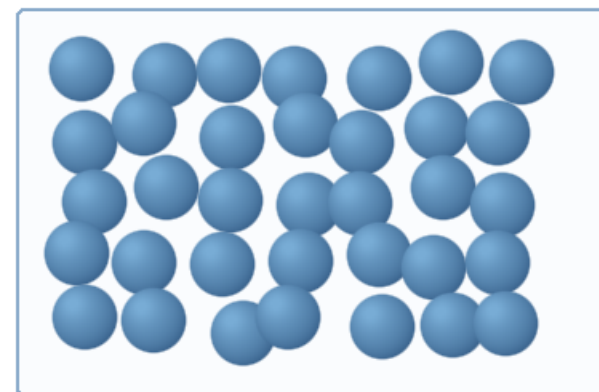
For a pure substance, chemical potential (μ) equals molar Gibbs energy (G_m).



Solid phase

$$\mu_{\text{solid}} = \mu_{\text{liquid}}$$

← Phase change →



Liquid phase

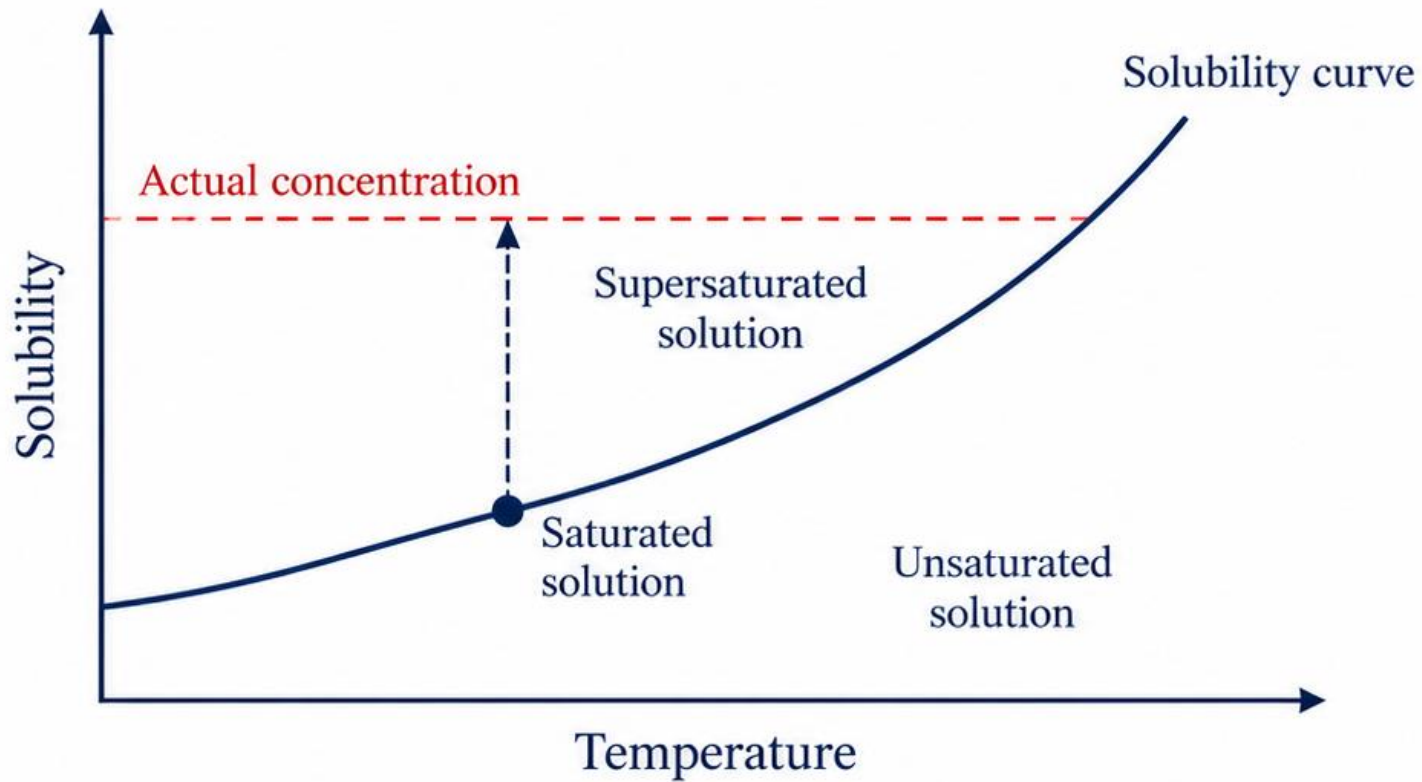
At equilibrium, transferring a small amount of substance between phases produces no net decrease in the system's Gibbs energy.

$\mu_{\text{solid}} < \mu_{\text{liquid}}$
Solid thermodynamically favoured

$\mu_{\text{liquid}} < \mu_{\text{solid}}$
Liquid thermodynamically favoured

Supersaturation: The Driving Force for Crystallisation

Supersaturation makes crystal formation thermodynamically favourable.

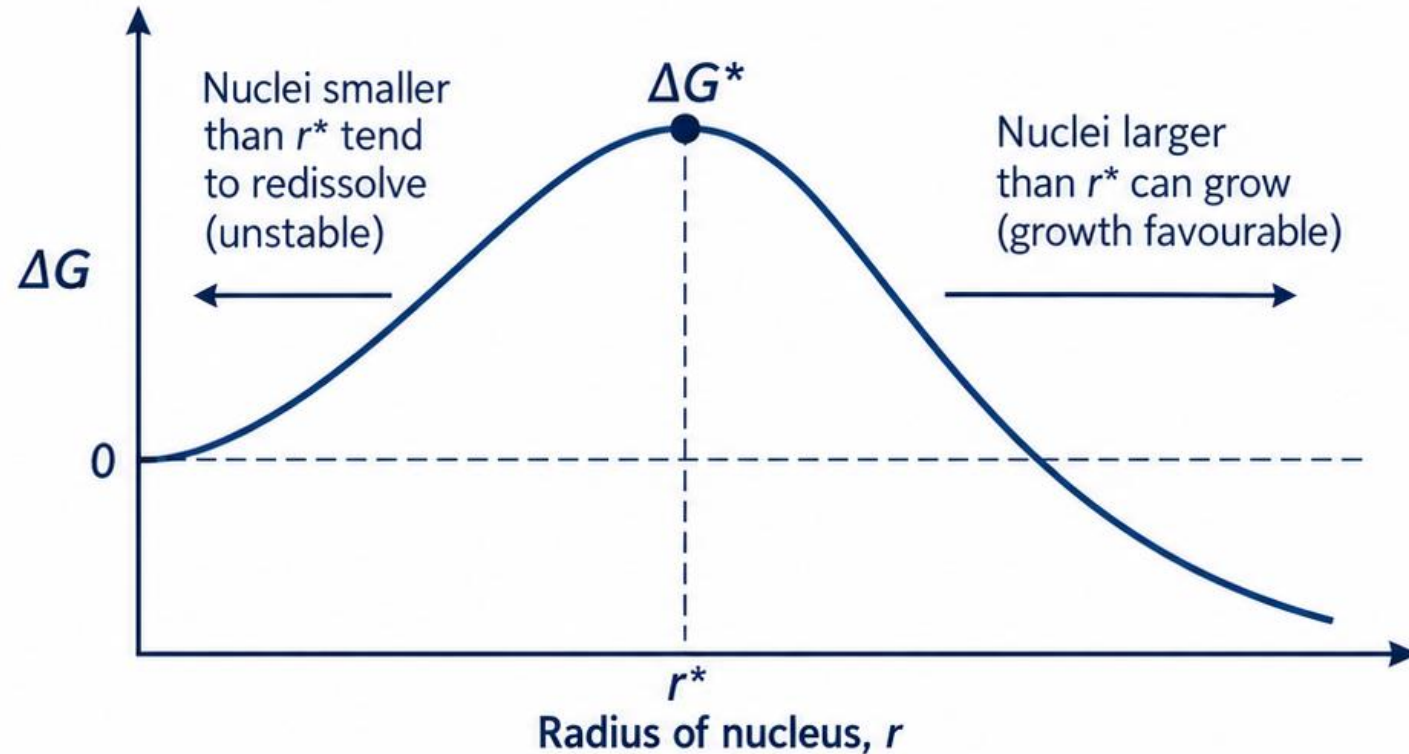


- At saturation, solution and crystals are in equilibrium.
- If the dissolved amount exceeds the equilibrium solubility, the solution is supersaturated.
- Supersaturation provides the thermodynamic driving force for crystallisation.

OME link: During manufacture, cooling or solvent removal can create supersaturation and promote crystallisation of energetic materials.

Why Doesn't Crystallisation Begin Immediately?

Nucleation barriers can delay crystallisation despite a favourable Gibbs energy change.

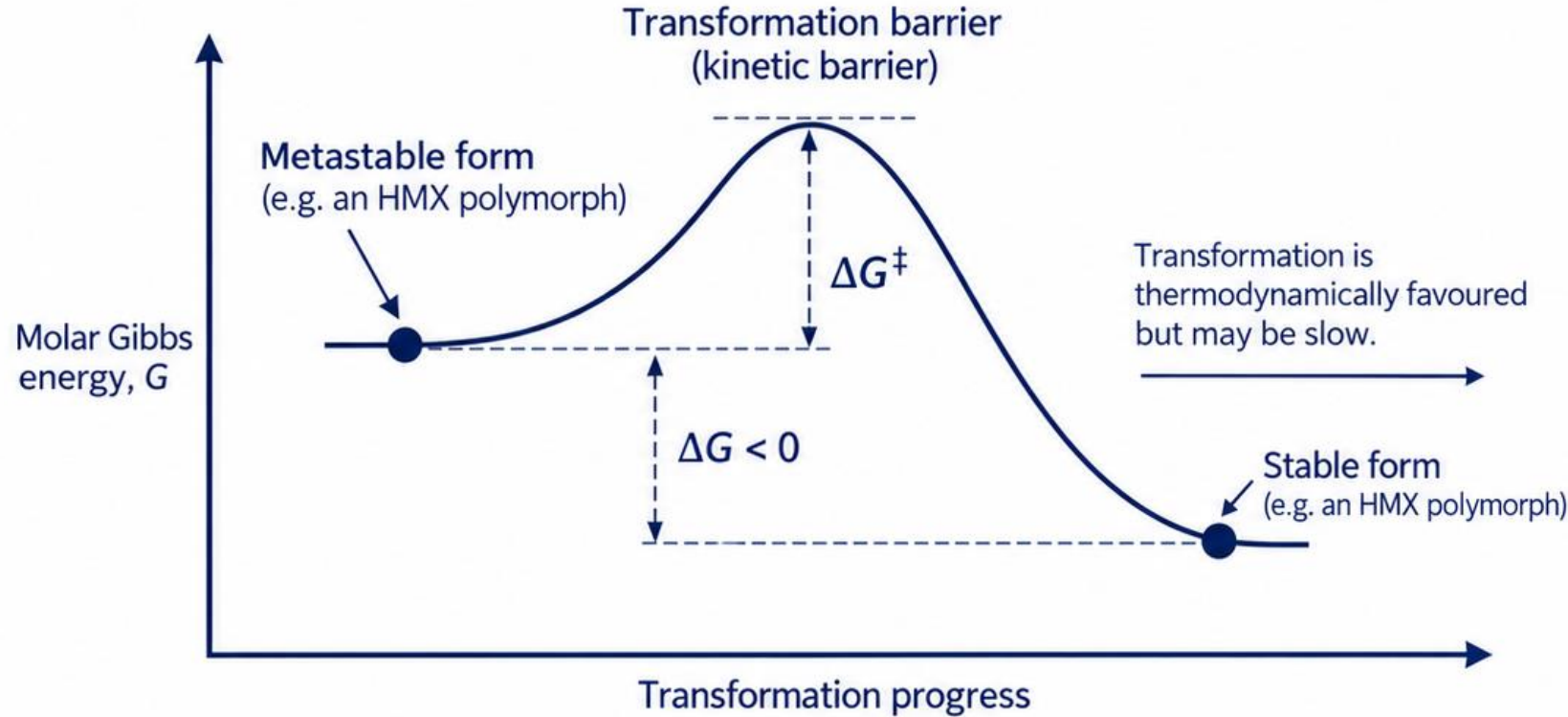


- Supersaturation provides a thermodynamic driving force for crystallisation.
- Forming a new crystal surface costs energy, so very small nuclei are unstable.
- Only nuclei larger than the critical size can continue to grow.

OME link: during manufacture or cooling, an energetic material may remain supersaturated until stable nuclei form.

Metastability in Energetic Materials

A less stable physical form can persist because transformation is kinetically hindered.



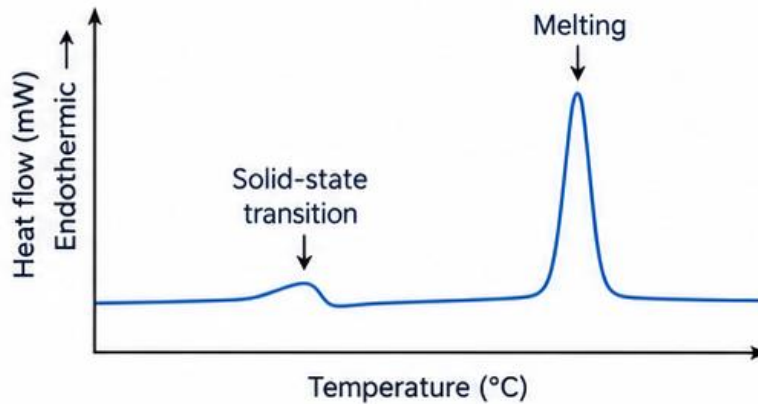
- A metastable form has higher Gibbs energy than the stable form under the same conditions.
- It can persist if the transformation barrier is large.
- In HMX, different polymorphs can exist, and the observed form depends on both thermodynamic stability and kinetics.

OME link: during manufacture, cooling or storage, an energetic material may retain a metastable crystalline form if transformation to the more stable form is kinetically hindered.

Experimental Evidence of Phase Behaviour

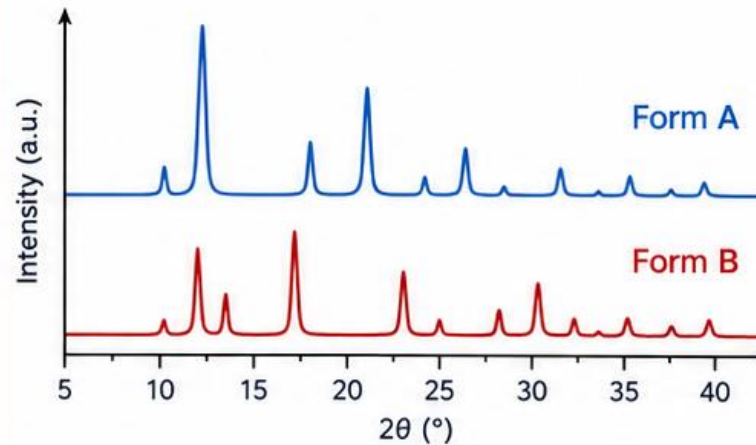
DSC, PXRD and microscopy provide complementary evidence of physical states and transformations.

Differential Scanning Calorimetry (DSC)



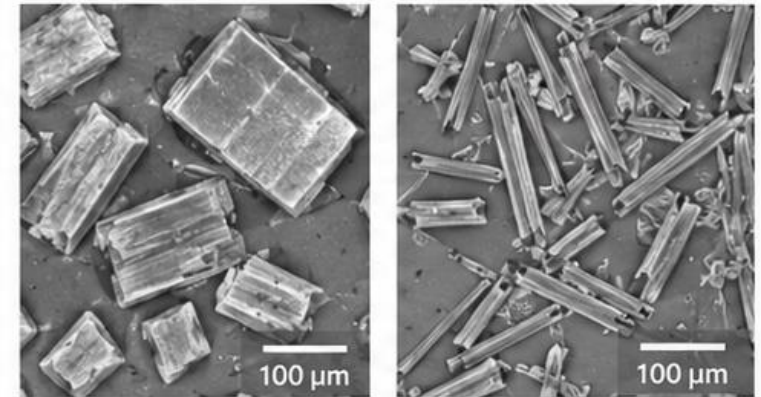
- Detects thermal events such as melting and some solid-state transitions.
- Helps identify whether a physical transformation occurs as temperature changes.

Powder X-ray Diffraction (PXRD)



- Diffraction patterns identify crystalline phases.
- Different polymorphs give different peak positions and intensities.

Microscopy



- Reveals particle shape, size and visible morphological change.
- Useful supporting evidence, but does not by itself prove phase identity.

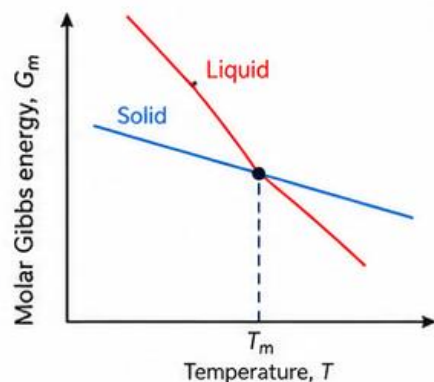
OME link: combining DSC, PXRD and microscopy helps determine whether an energetic material has changed physical form during manufacture or storage.



Part 3 Summary

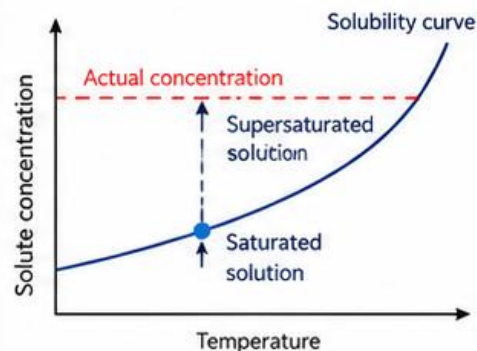
Thermodynamics, kinetics and experimental evidence help us understand phase behaviour and the solid state.

1. Phase stability



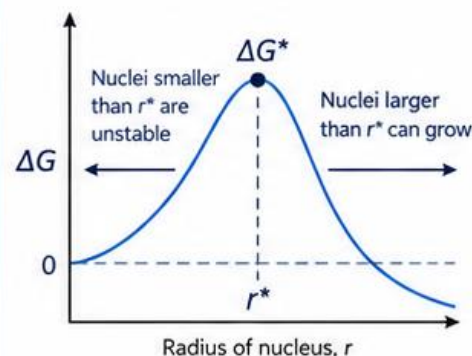
- The phase with lower G_m is thermodynamically favoured.
- At T_m , $\mu_{\text{solid}} = \mu_{\text{liquid}}$ and the two phases coexist.
- Below T_m : solid favoured.
- Above T_m : liquid favoured.

2. Supersaturation



- Supersaturation occurs when the dissolved amount exceeds the equilibrium solubility.
- Supersaturation provides a thermodynamic driving force for crystallisation.
- Can be created by cooling or removing solvent.

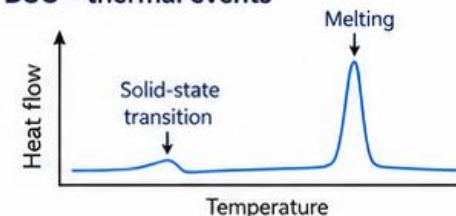
3. Nucleation barrier



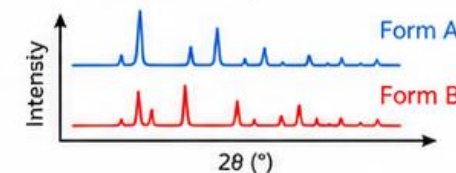
- Forming a new crystal surface costs energy.
- Very small nuclei are unstable and tend to redissolve.
- Only nuclei larger than the critical size, r^* , can grow.
- This kinetic barrier can delay crystallisation.

4. Experimental evidence

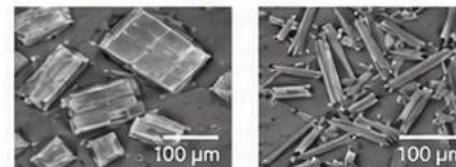
DSC – thermal events



PXRD – crystalline phases



Microscopy – crystal morphology



5. Overall picture

- Thermodynamics predicts which phase is favoured.
- Kinetic barriers, such as nucleation, can delay transformation.
- Supersaturation provides the driving force for crystallisation.
- Experimental techniques (DSC, PXRD and microscopy) provide complementary evidence of physical states and transformations.
- This understanding is essential for energetic materials, where the physical form can influence processing, storage and performance.



Key message: Phase behaviour results from the interplay of thermodynamics, kinetics and experimental evidence. All three are needed to understand and control the solid state of energetic materials.