Materials Chemistry II
-Applications 1-

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Outline

1. Understanding processes&materials based on G(x,T,p)
QUALITATIVE APPLICATION OF MC II

2. Modelling G(x,T,p) based on theory&experiment
QUALITATIVE → QUANTITATIVE

3. Modelling processes&materials based on G(x,T,p)
QUANTITATIVE APPLICATION OF MC II

You want to be an engineer.

Why?

Association of German Engineers (VDI): Fundamentals of engineering ethics

„Ingenieurinnen und Ingenieure bekennen sich zu ihrer Bringpflicht für sinnvolle technische Erfindungen und Lösungen.“

“Engineers are committed to delivering sensible technology and technical solutions.“

https://www.vdi.de/bildung/ethische-grundsaetze/ethische-grundsaetze/

In order to develop sensible technology and technical solutions as a metallurgical engineer you need to be able to **apply** the **fundamentals of thermodynamics**.

“Sensible technology”:
What thermodynamic property will tell you whether a process can occur spontaneously?

A) ΔH_{system}

B) ΔS_{system}

C) ΔG_{system}

D) ΔV_{system}

“Sensible technology”:
What thermodynamic property will tell you whether a process can occur spontaneously?

A) ΔH_{system}

B) ΔS_{system}

[✓ C) ΔG_{system}]

D) ΔV_{system}

“Sensible technology”: What thermodynamic property will tell you whether a process can occur spontaneously?

A) ΔH_{system}

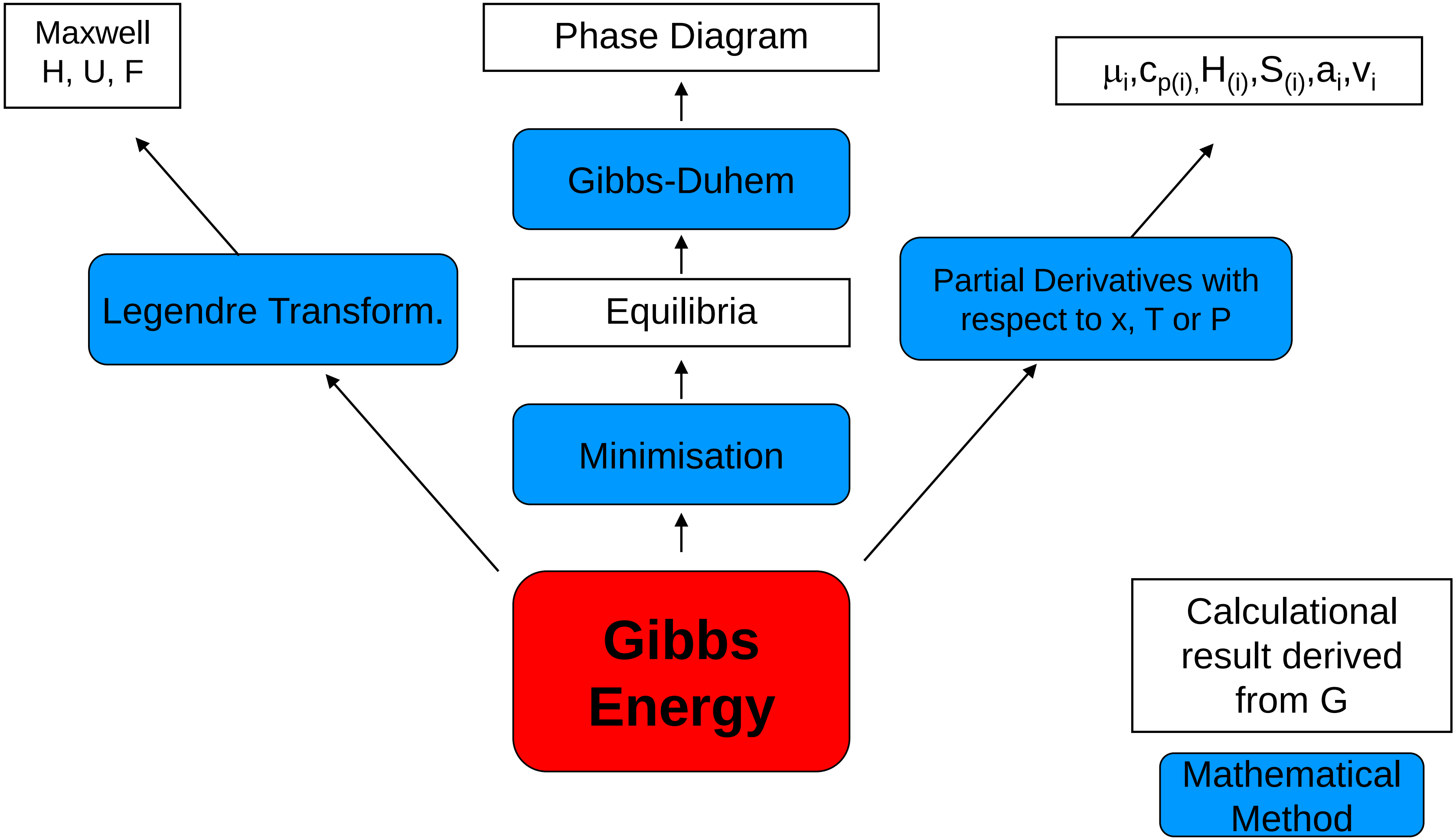
B) ΔS_{system}

C) $\boxed{\Delta G_{system} < 0}$

We need to describe $G(T,p,X_i)$!

D) ΔV_{system}

Computational thermodynamics



Maxwell
H, U, F

Phase Diagram

$\mu_i, c_{p(i)}, H_{(i)}, S_{(i)}, a_i, v_i$

Gibbs-Duhem

Legendre Transform.

Equilibria

Partial Derivatives with respect to x, T or P

Minimisation

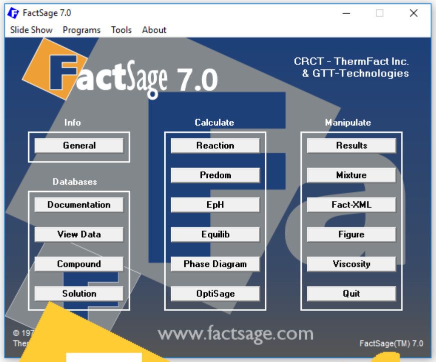
Gibbs Energy

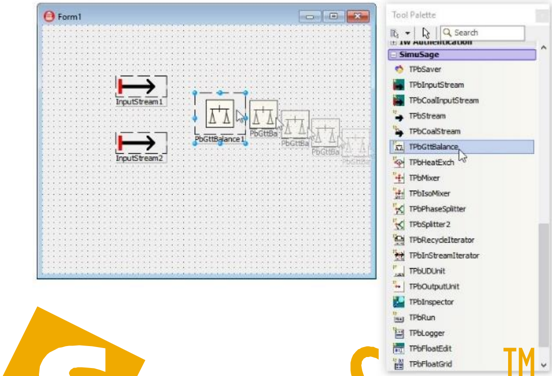
Calculational result derived from G

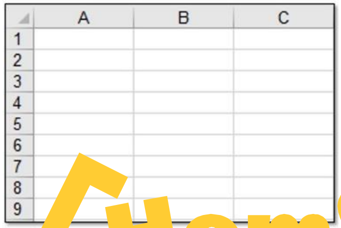
Mathematical Method

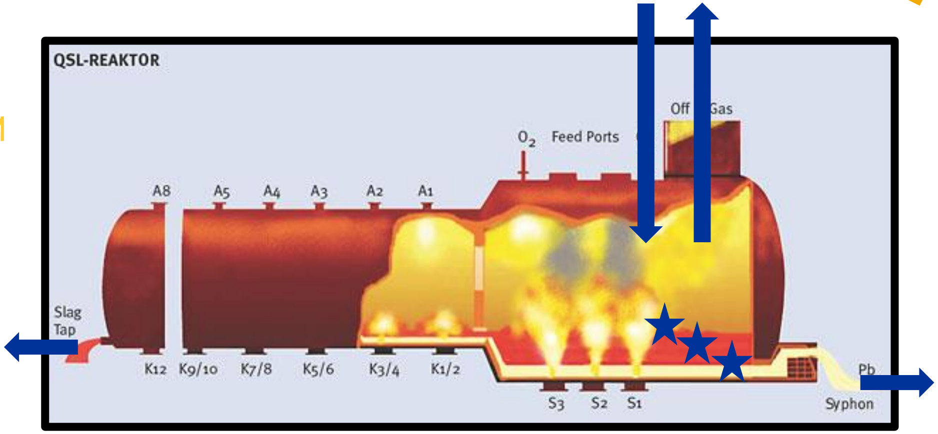
Alternative software solutions: ThermoCalc, Pandat, JMatPro, OpenCalphad, MTDATA…

Software using Gibbs energy minimization @





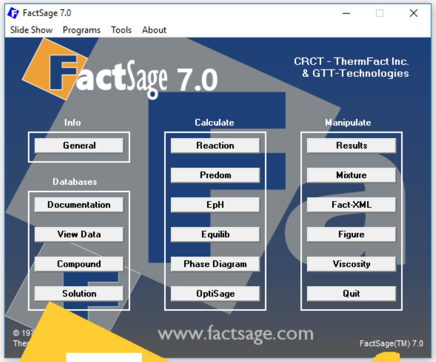


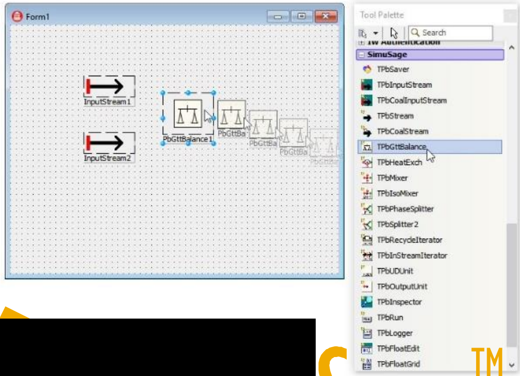


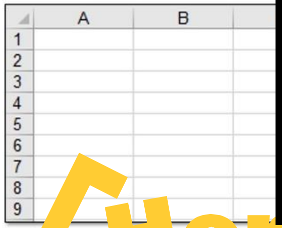
www.berzelius.de/berzelius/bilder/qsl-reaktor.jpg

Alternative software solutions: ThermoCalc, Pandat, JMatPro, OpenCalphad, MTDATA…

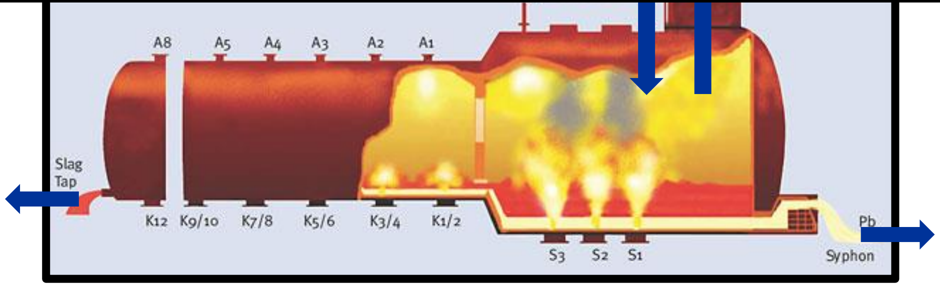
Software using Gibbs energy minimization @







ALL OF THESE APPLICATIONS NEED THERMODYNAMIC DATA G(x,T,p)!



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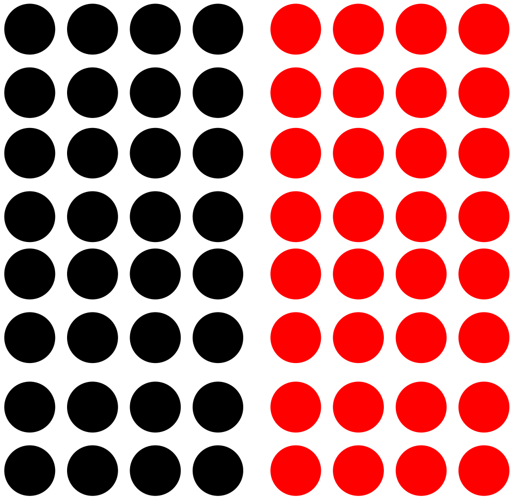
3. Modelling processes&materials based on G(x,T,p)

QUANTITATIVE APPLICATION OF MC II

Strategy:

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

Think about bonds & configurations

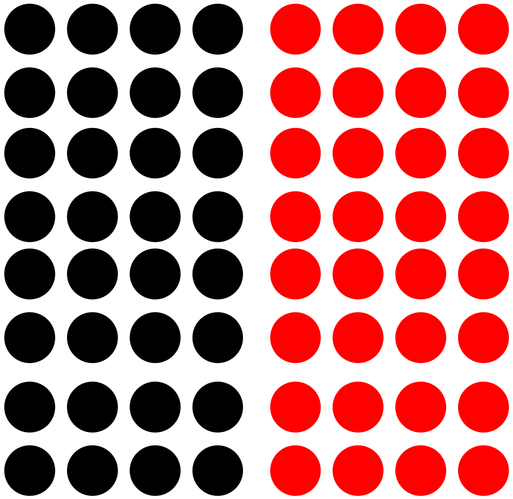


mechanical mixture
(two powders)

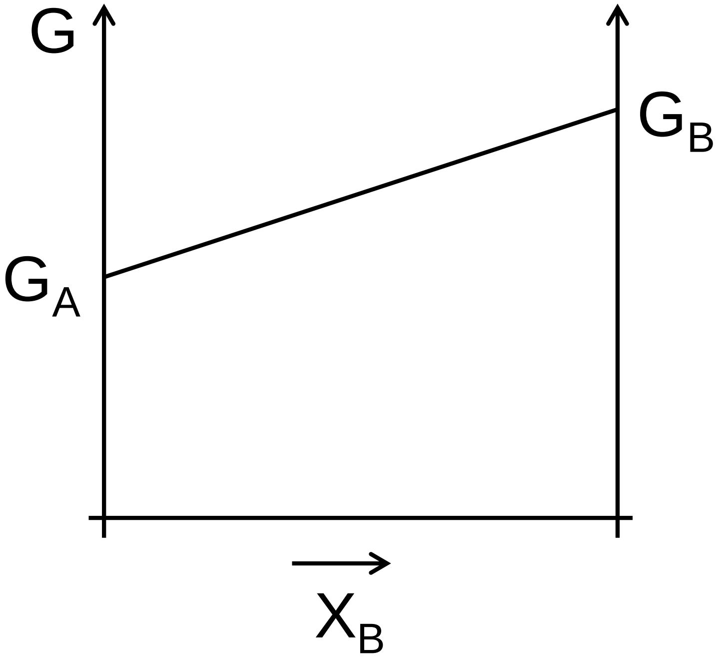
Mechanical mixture

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations



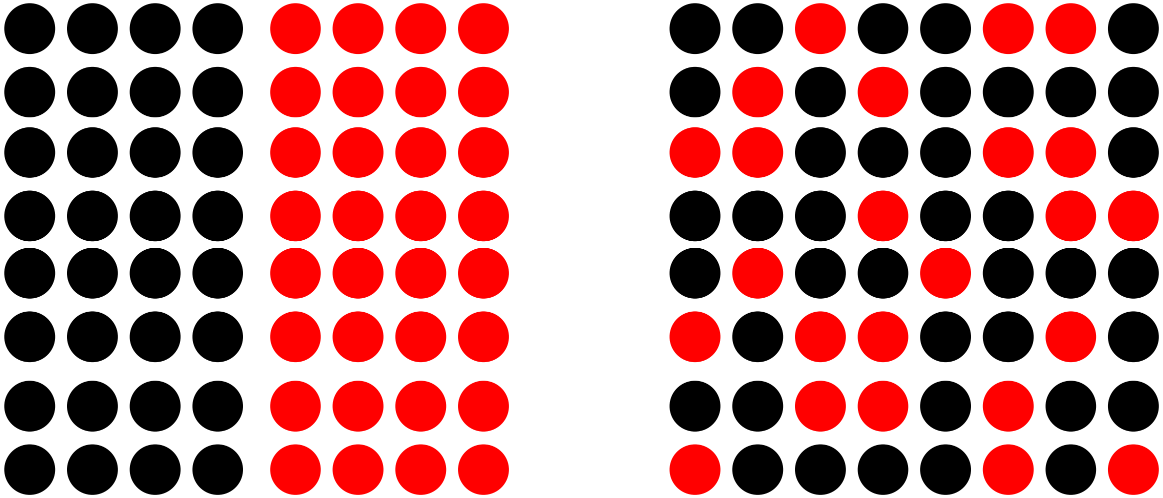
$$G_{total} = X_A\, G_A + X_B\, G_B$$



Strategy:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations



mechanical mixture
(two powders)

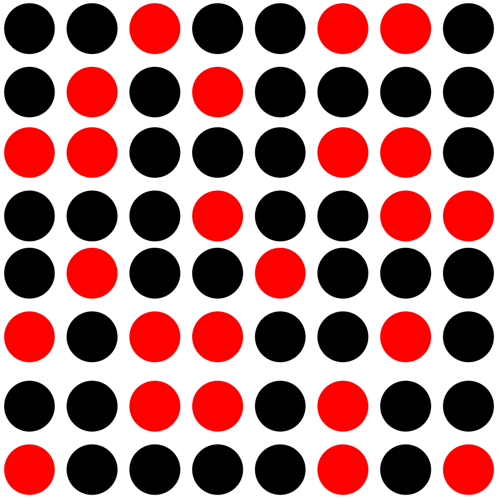
→

ideal/regular solution
mixed

Ideal solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations



Bonds:

Definition of ideal solution: Bond energy ε of A-B is the same as the average of A-A and B-B.

→ No change in energetics → $\Delta H_{mix} = 0$

Configurations:

Statistical distribution of atoms

→ Large entropy gain → $\Delta S_{mix} > 0$

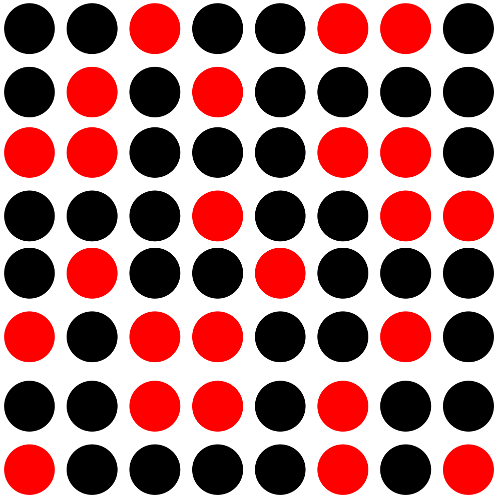
$$\begin{aligned} G_{total} &= X_A G_A + X_B G_B + \Delta G_{mix} \\ &= X_A G_A + X_B G_B - T\Delta S_{mix} \end{aligned}$$

→ what is ΔS_{mix}?

Ideal solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

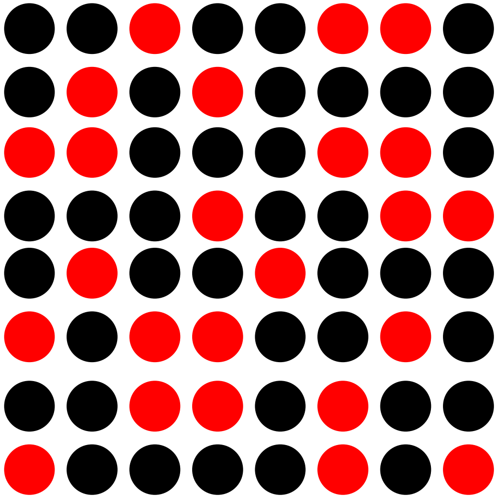
$$\Delta S_{mix} = S_{after} - S_{before}$$

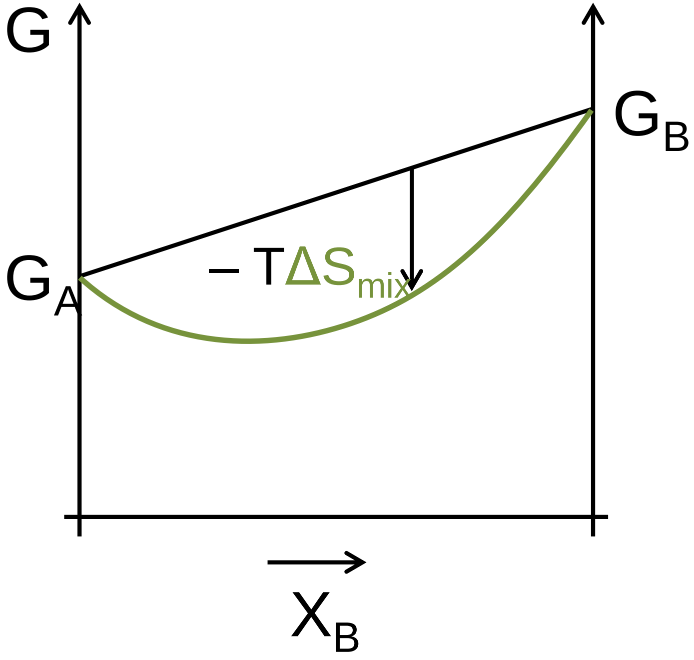


Ideal solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$G_{total} = X_A\, G_A + X_B\, G_B + RT\,(X_A \ln X_A + X_B \ln X_B)$$

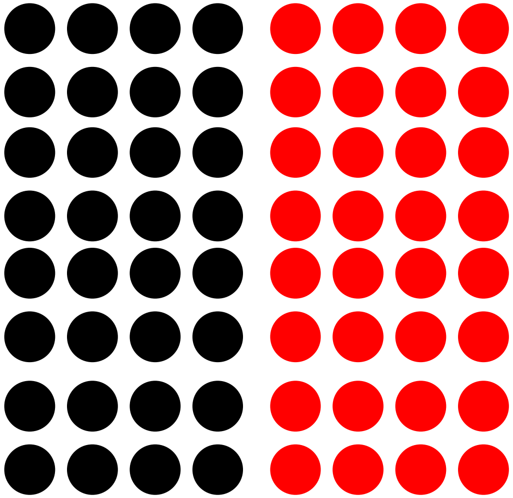


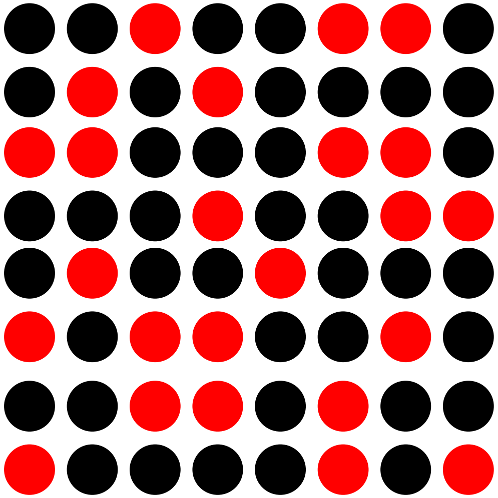


Strategy:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations





mechanical mixture
(two powders)

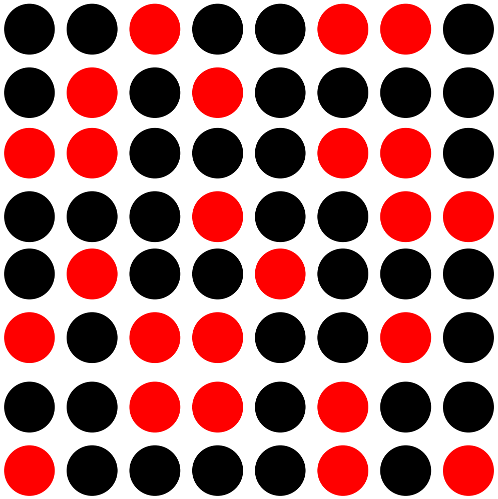
→

ideal/**regular solution**
mixed

Regular solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations



Bonds:

Bond energy ε of A-B is NOT the same as the average of A-A and B-B.

→ Change in energetics → **$\Delta H_{mix} \neq 0$**

Configurations:

Statistical distribution of atoms

→ High entropy gain → $\Delta S_{mix} > 0$

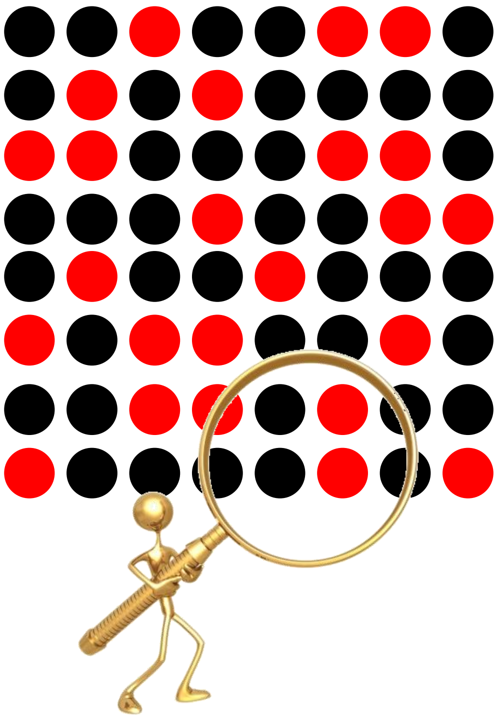
$$\begin{aligned} G_{total} &= X_A\, G_A + X_B\, G_B + \Delta G_{mix} \\ &= X_A\, G_A + X_B\, G_B + \Delta H_{mix} - T\Delta S_{mix,ideal} \end{aligned}$$

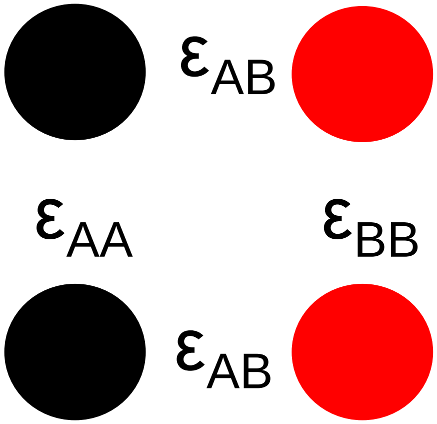
→ what is ΔH_{mix}?

Regular solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations



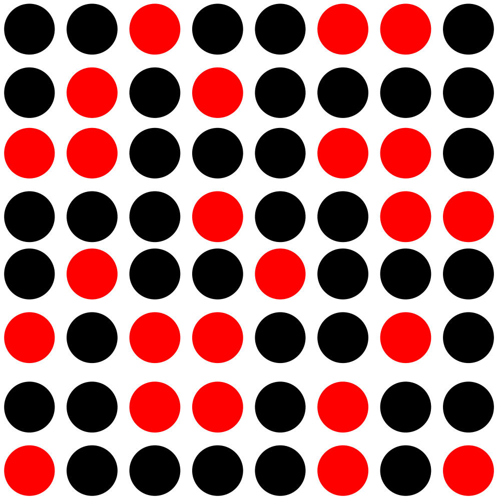


ε_{AB}: A-B bond energy

What is the total bond energy before/after mixing?

→ ΔH_{mix}

Regular solution



$\Delta H_{mix} = \Omega * X_A * X_B$

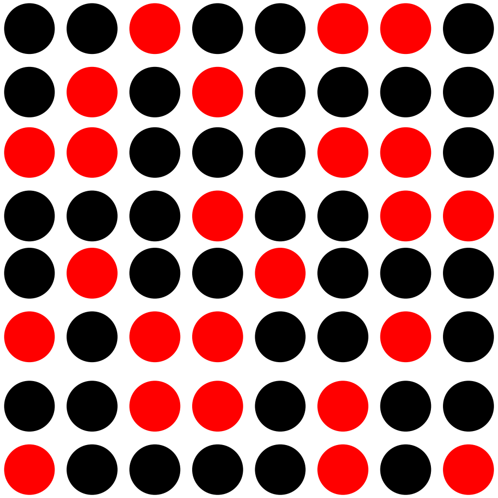
$\Omega = N_a * z * \varepsilon = N_a * z * (\varepsilon_{AB} - ½ (\varepsilon_{AA} + \varepsilon_{BB}))$

Ω: Interaction parameter

If **A-B** bonds are energetically **more favourable** than the mean of A-A and B-B bonds, Ω and ΔH_{mix} will be **negative**.

If **A-B** bonds are energetically **less favourable** than the mean of A-A and B-B bonds, Ω and ΔH_{mix} will be **positive**.

Regular solution



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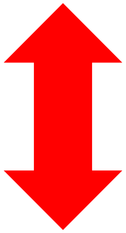


CONTRADICTION

Configurations:

Statistical distribution of atoms

→ High entropy gain → $\Delta S_{mix} > 0$

Limitations of the regular solution model

ΔS_{mix}: random mixing of A and B, i.e. A-A, B-B and A-B bonds must have same energy.

ΔH_{mix}: 2 A-B bonds do not have the same energy as one A-A and one B-B bond.

$\Omega = N_a z[\varepsilon_{AB} - ½(\varepsilon_{AA} + \varepsilon_{BB})]$

$\Omega < 0$: tendency towards ordering

$\Omega > 0$: tendency towards clustering

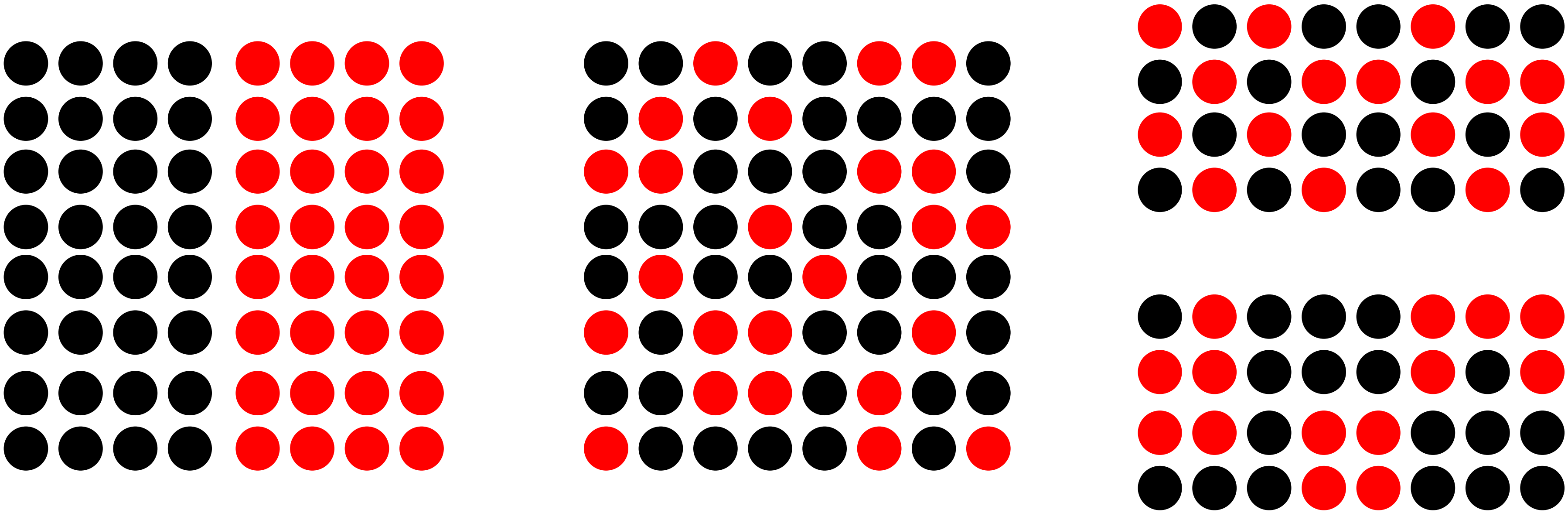
Ω has to be small, otherwise A and B will **not** be randomly mixed!

(→ different ΔS_{mix} and ΔH_{mix}!)

Strategy:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations



mechanical mixture
(two powders)

→

ideal/regular solution
mixed

→

real solution
ordering/clustering

What happens if Ω is significantly different from 0?

$\Omega < 0$

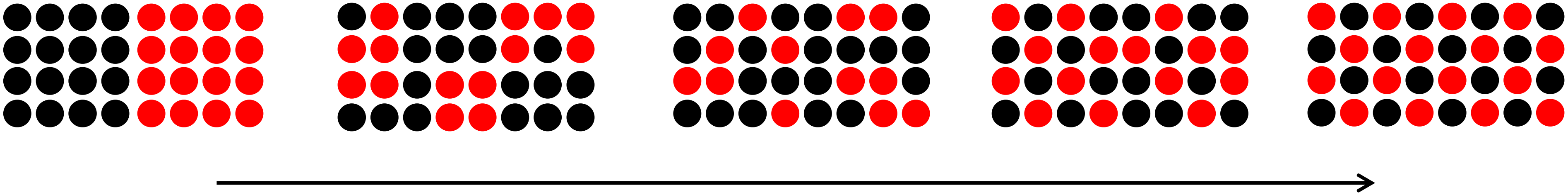
What happens if Ω is significantly different from 0?

$\Omega < 0$

Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}


Probability of A-B-pair increases

P_{AB}

ΔH_{mix}

ΔS_{mix}

What happens if Ω is significantly different from 0?

$\Omega < 0$

Example: Solution of 50% A and 50% B

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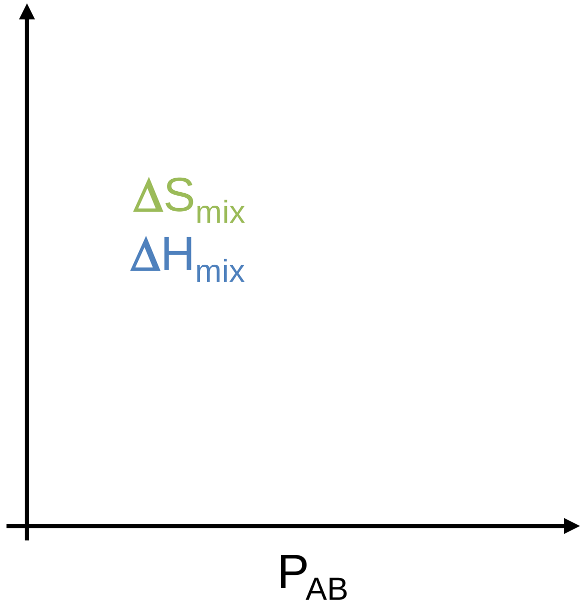
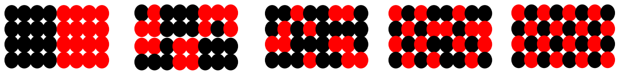




Probability of A-B-pair increases

$P_{AB} = 0$
$\Delta H_{mix} = 0$
$\Delta S_{mix} = 0$

$P_{AB} = 2{*}X_A{*}X_B = 0.5$
$\Delta H_{mix} = 0.25\ \Omega$
$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$

$P_{AB} = 1$
$\Delta H_{mix} = 0.5\ \Omega$
$\Delta S_{mix} = 0$

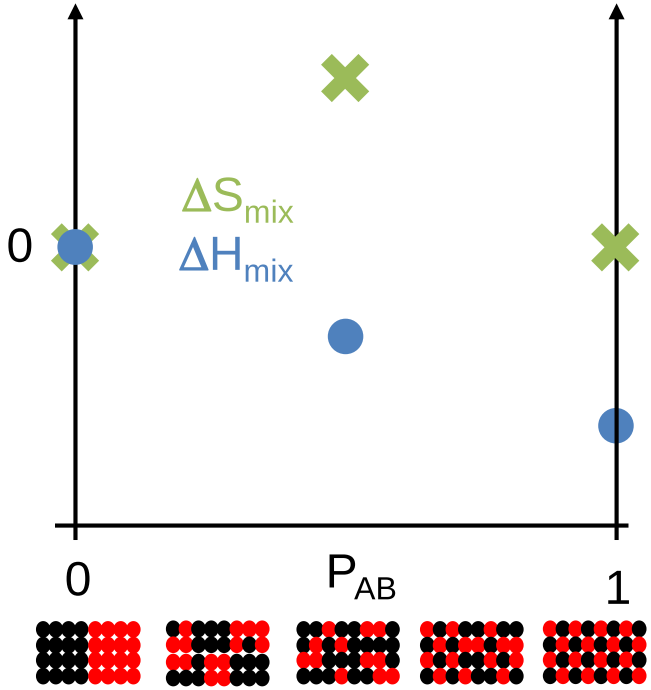
What happens if Ω is significantly different from 0?

$\Omega < 0$

Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}



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$P_{AB} = 1$
$\Delta H_{mix} = 0.5\ \Omega$
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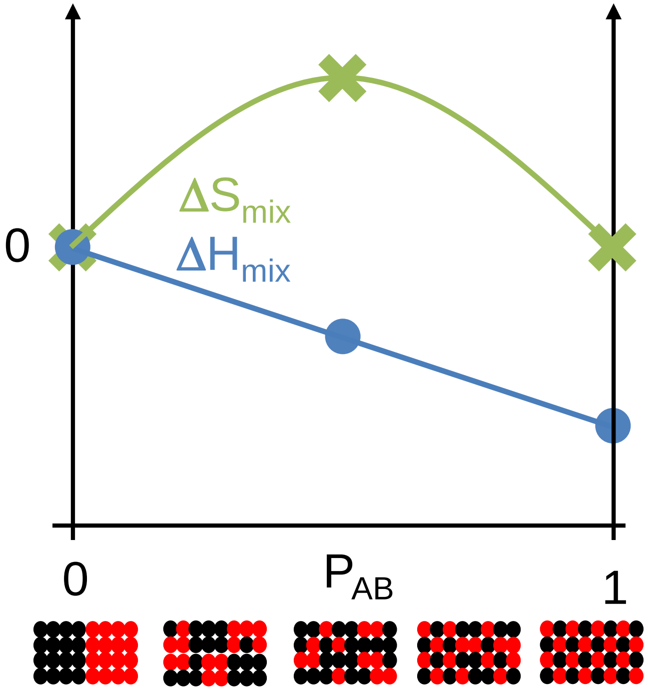
What happens if Ω is significantly different from 0?

$\Omega < 0$

Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}



Probability of A-B-pair increases

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$P_{AB} = 1$
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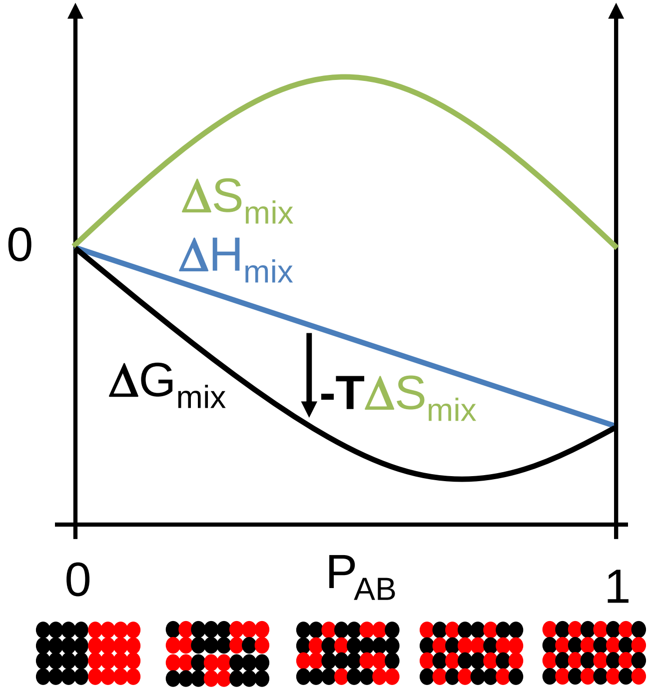
$\Omega < 0$

Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}



Probability of A-B-pair increases

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$\Delta S_{mix} = 0$

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$\Delta H_{mix} = 0.25\ \Omega$
$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$

$P_{AB} = 1$
$\Delta H_{mix} = 0.5\ \Omega$
$\Delta S_{mix} = 0$

What happens if Ω is significantly different from 0?

Ω < 0

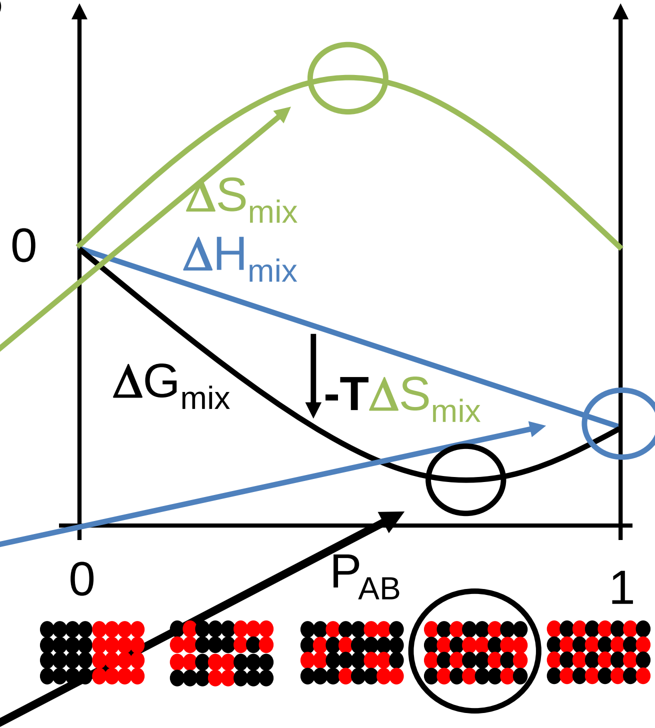
Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}

ΔS_{mix} maximizes when # of A-B bonds $= 2*X_A*X_B$

ΔH_{mix} minimizes with maximum number of A-B bonds



ΔG_{mix} minimizes between 0.5 and 1!

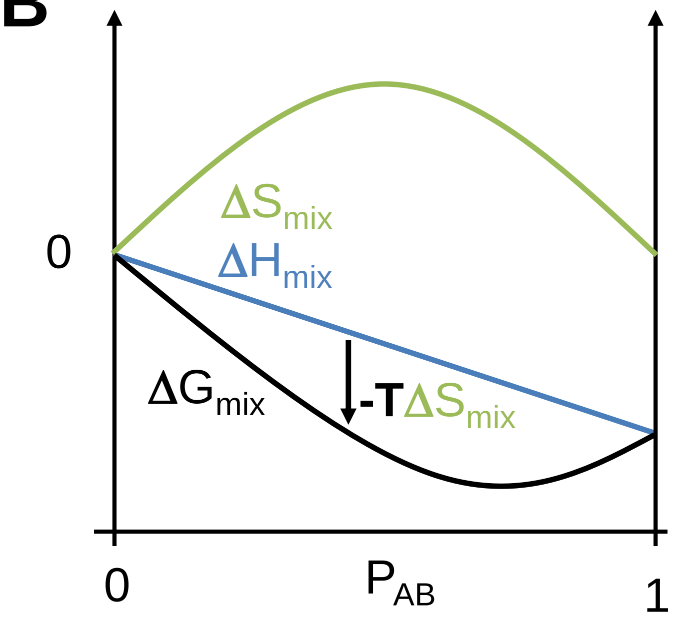
What happens if Ω is significantly different from 0?

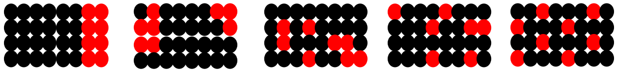
$\Omega < 0$

Example: Solution of **75% A** and **25% B**

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}





What happens if Ω is significantly different from 0?

$\Omega < 0$

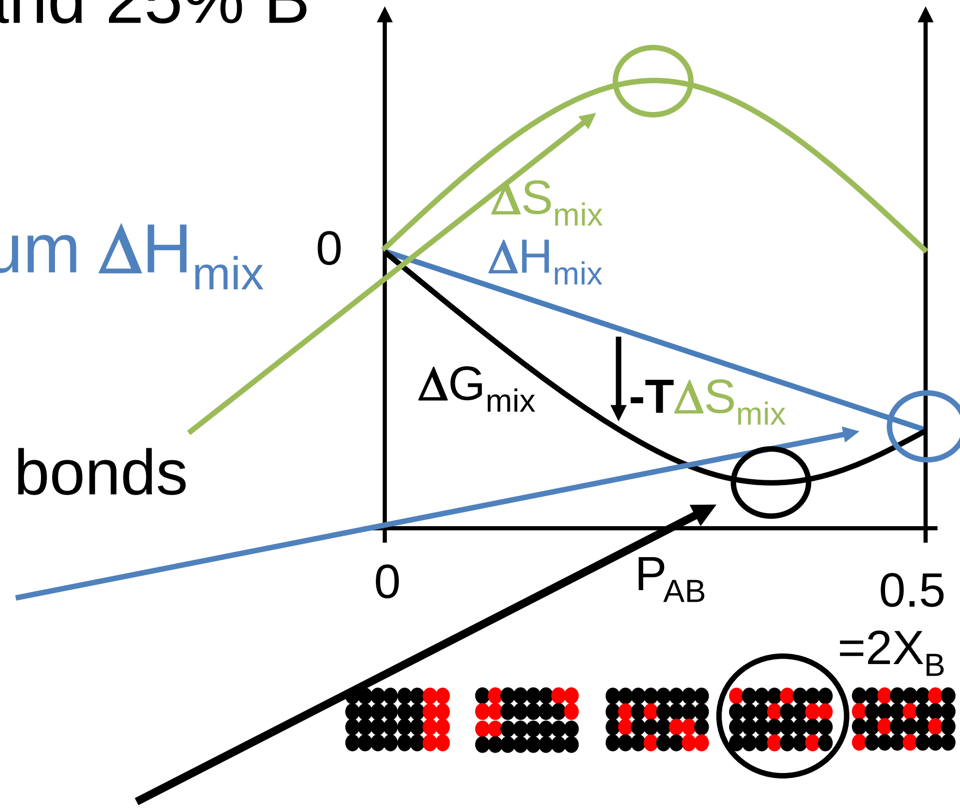
Example: Solution of 75% A and 25% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}

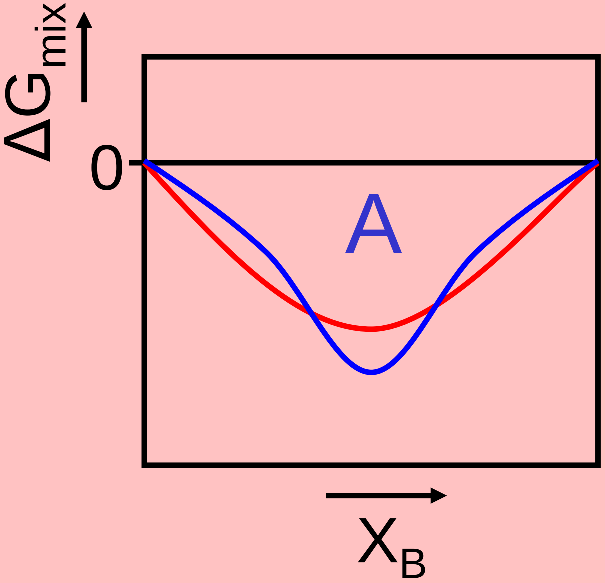
ΔS_{mix} maximizes when # of A-B bonds $= 2*X_A*X_B$

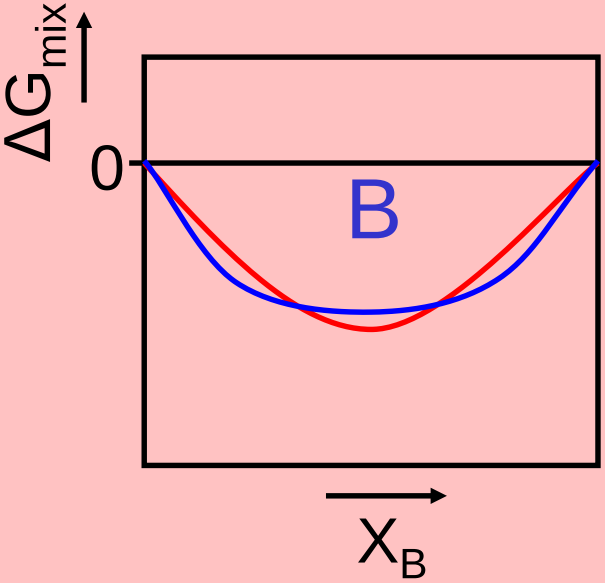
ΔH_{mix} minimizes with maximum number of A-B bonds

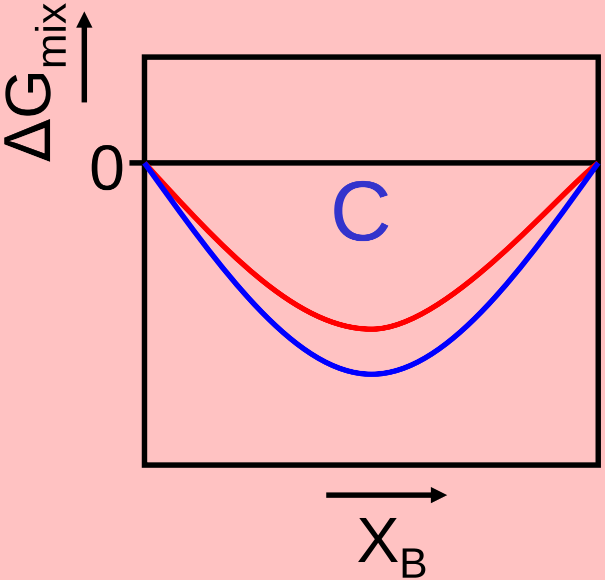


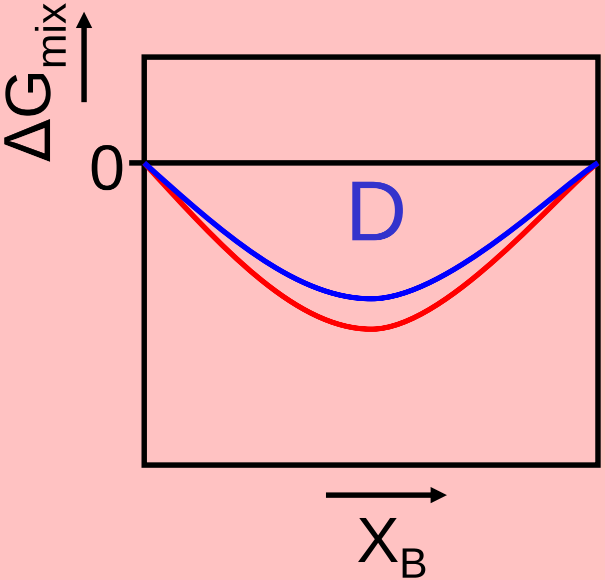
ΔG_{mix} minimizes between $P_{AB,random}$ and $P_{AB,max}$!

Schematically: How does ΔG_{mix}^{real} compare to $\Delta G_{mix}^{regular}$ for $\boldsymbol{\Omega < 0}$?

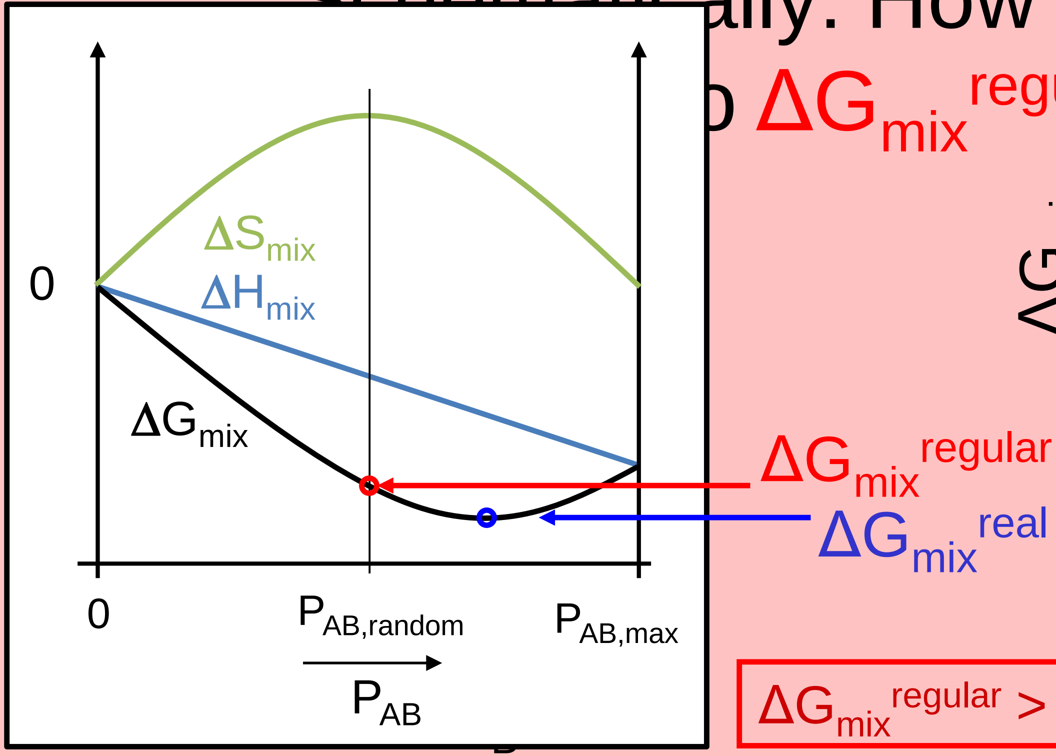


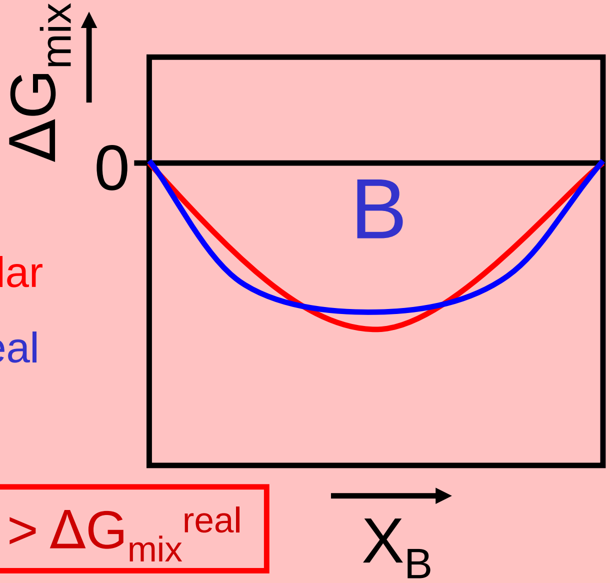




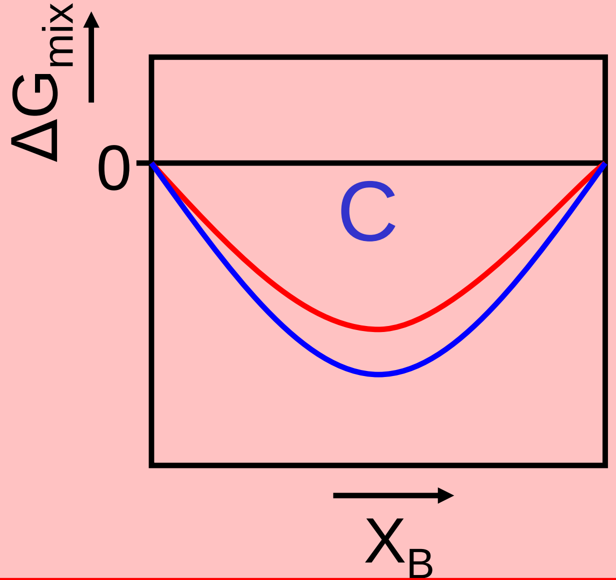


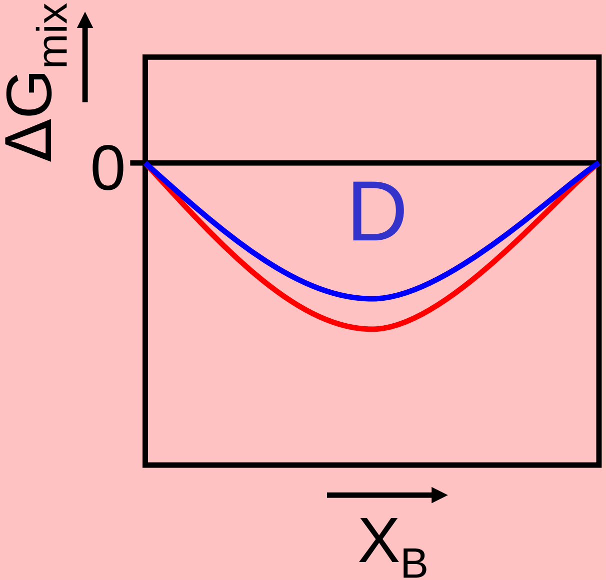
Schematically: How does ΔG_{mix}^{real} … o $\Delta G_{mix}^{regular}$ for **$\Omega < 0$**?





$\Delta G_{mix}^{regular} > \Delta G_{mix}^{real}$





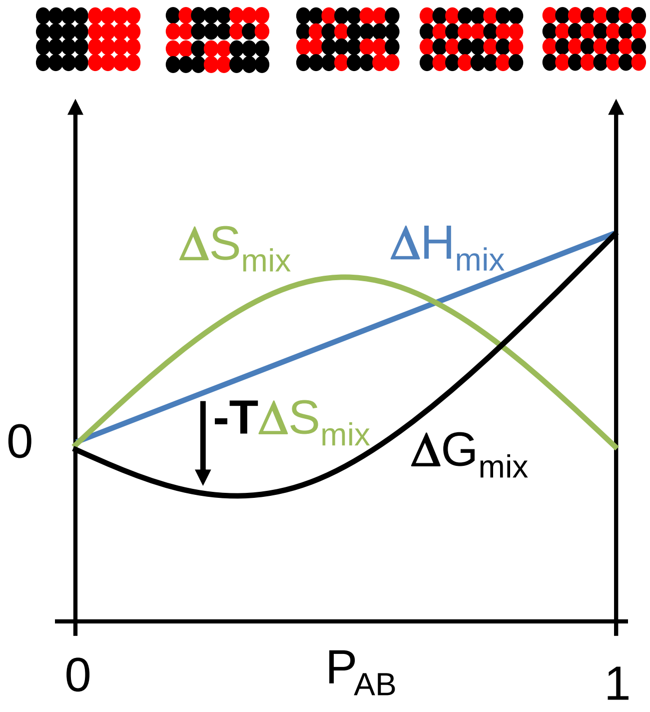
What happens if Ω is significantly different from 0?

Ω > 0

Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}

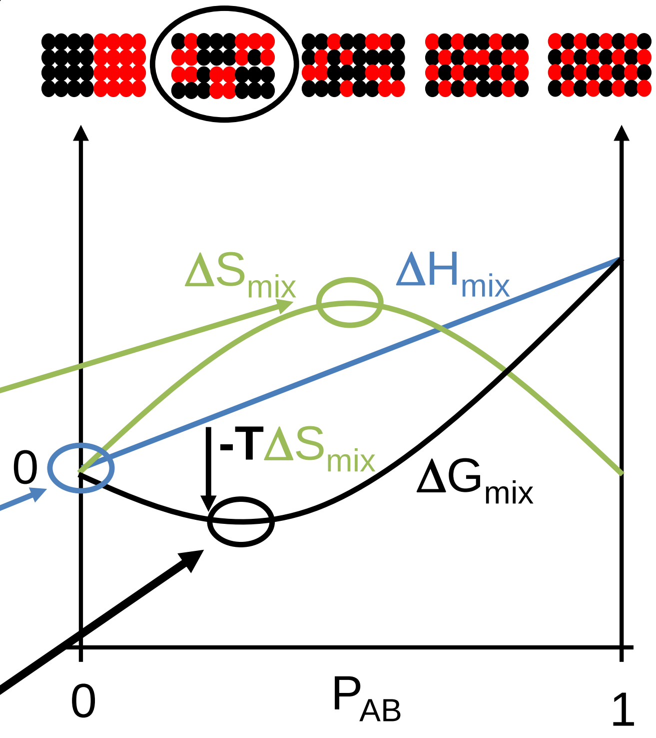


What happens if Ω is significantly different from 0?

$\Omega > 0$

Example: Solution of 50% A and 50% B

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$



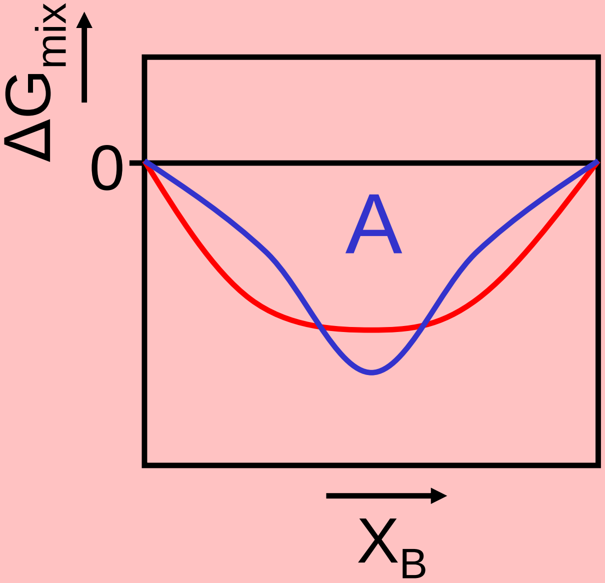
- ΔG_{mix} minimizes with minimum ΔH_{mix} and maximum ΔS_{mix}

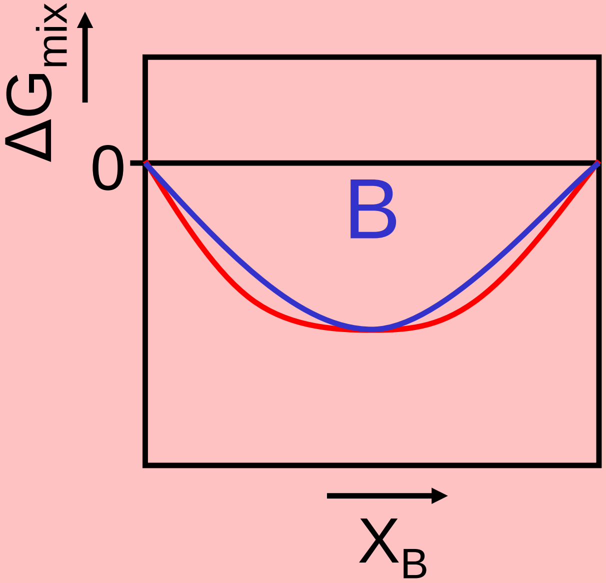
ΔS_{mix} maximizes when # of A-B bonds $= 2 * X_A * X_B$

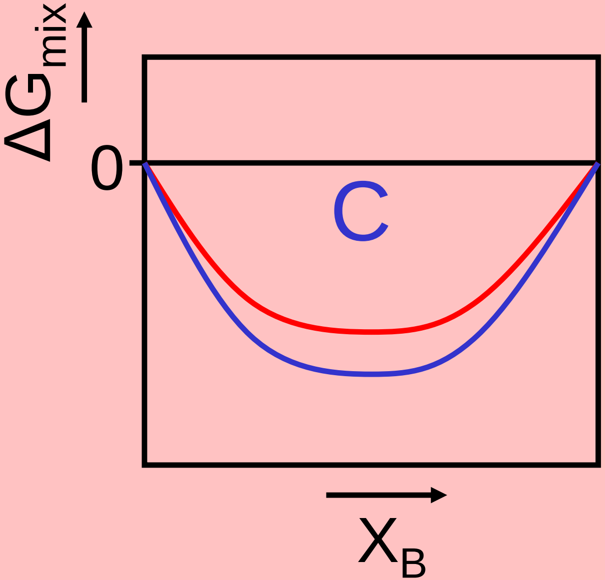
ΔH_{mix} minimizes with minimum number of A-B bonds

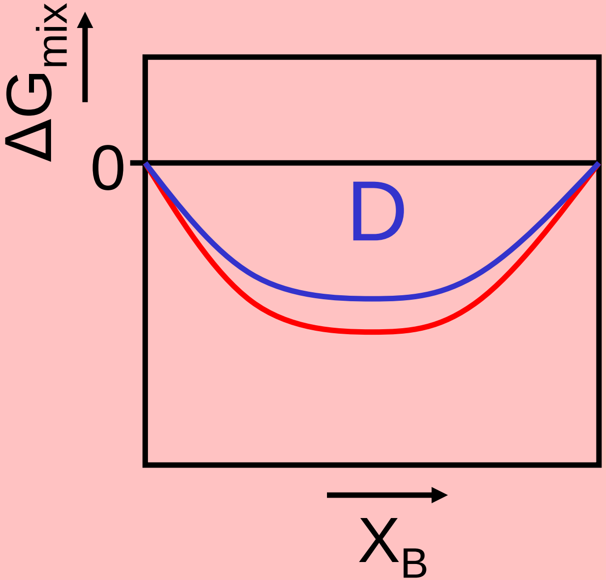
ΔG_{mix} minimizes between 0 and 0.5!

Schematically: How does ΔG_{mix}^{real} compare to $\Delta G_{mix}^{regular}$ for $\boldsymbol{\Omega > 0}$?

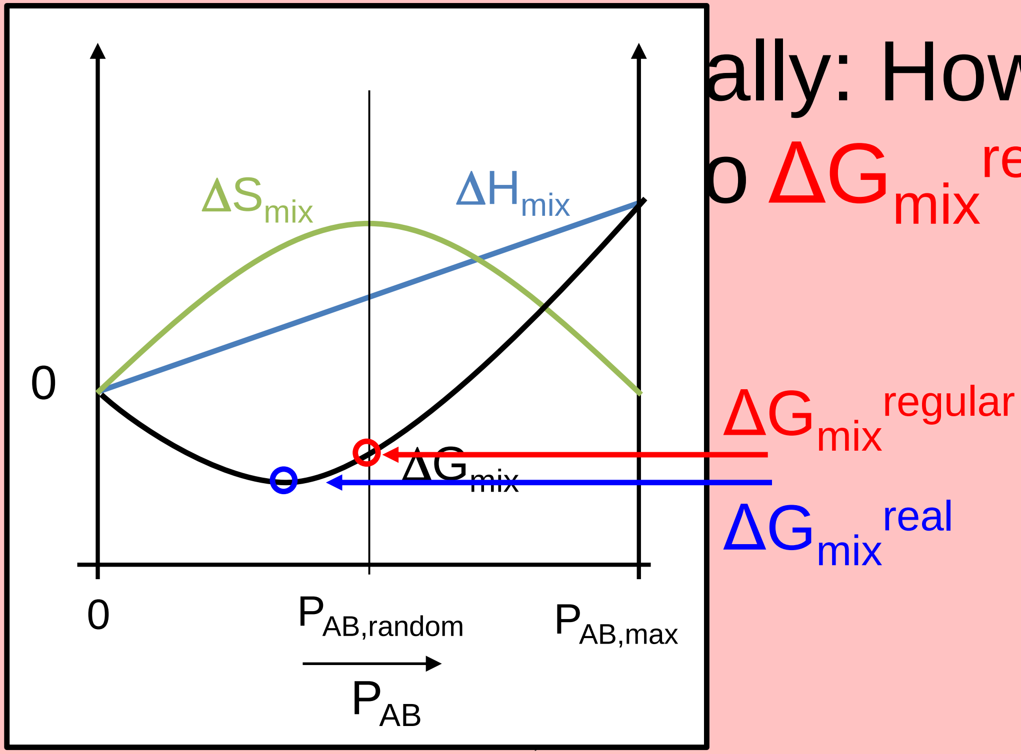


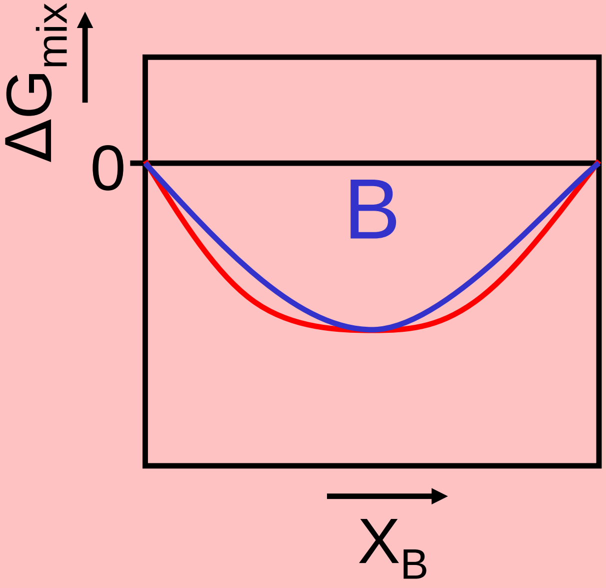




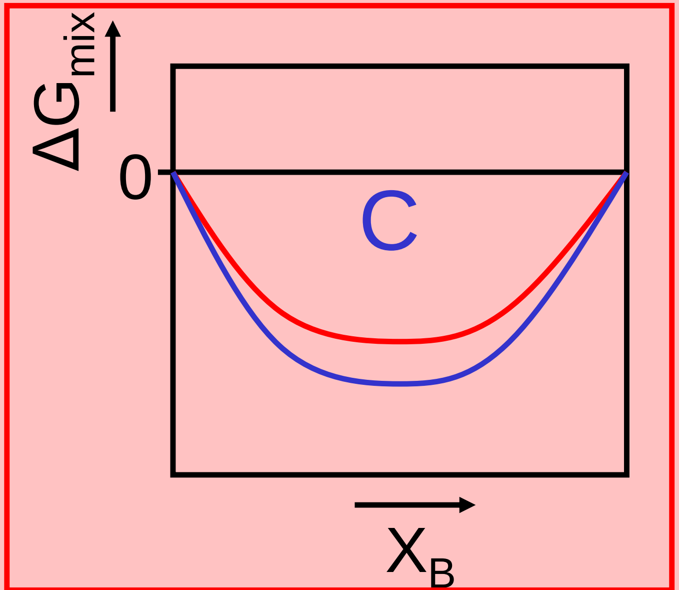


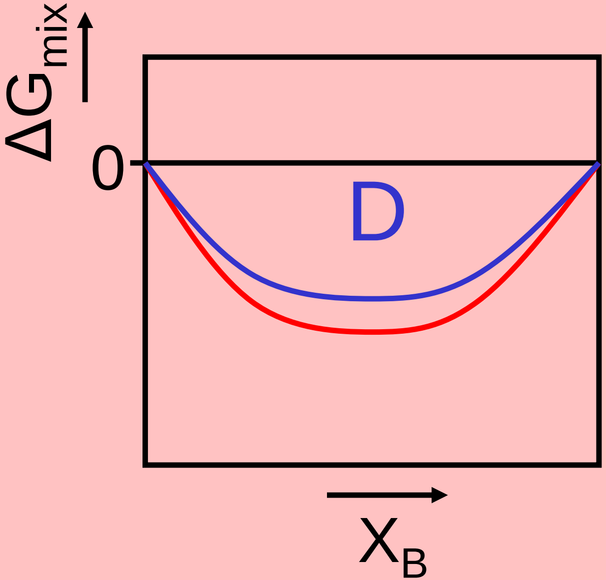
ally: How does ΔG_{mix}^{real} o $\Delta G_{mix}^{regular}$ for **Ω > 0**?





X_B



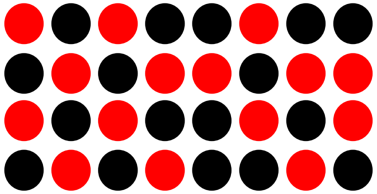


Strategy:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations

REAL SOLUTIONS

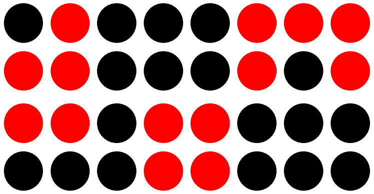


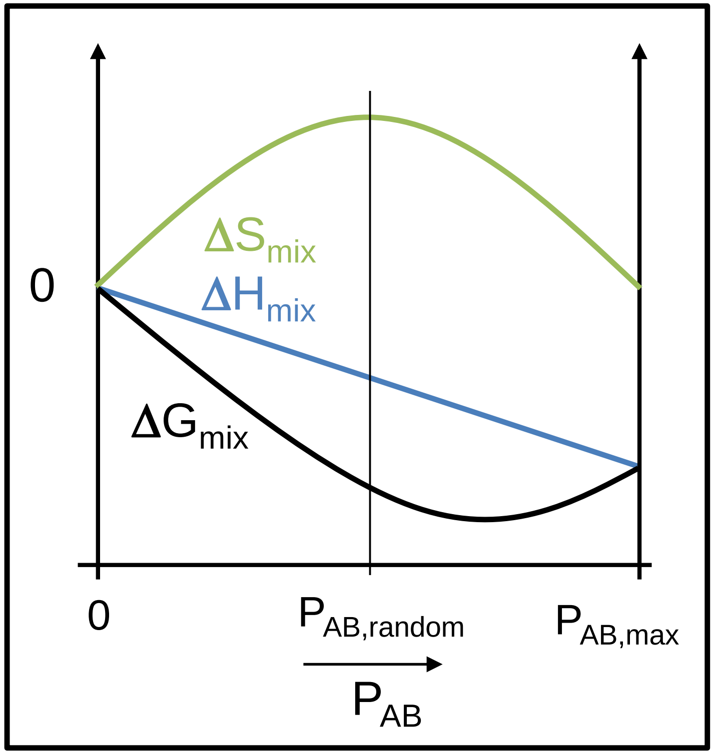
$\Omega<0$

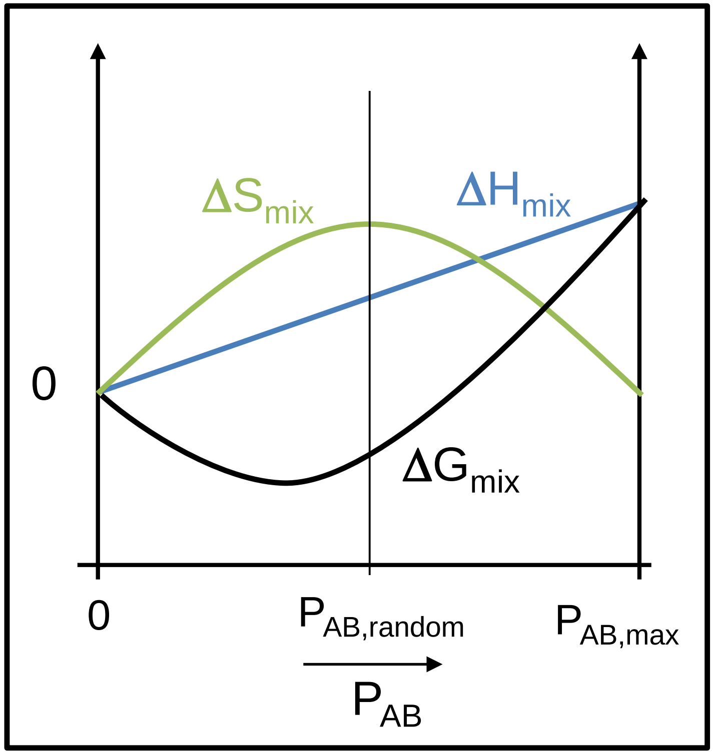
Ordering

$\Omega>0$

Clustering







Application: (Ti,Al)N coatings for cutting tools

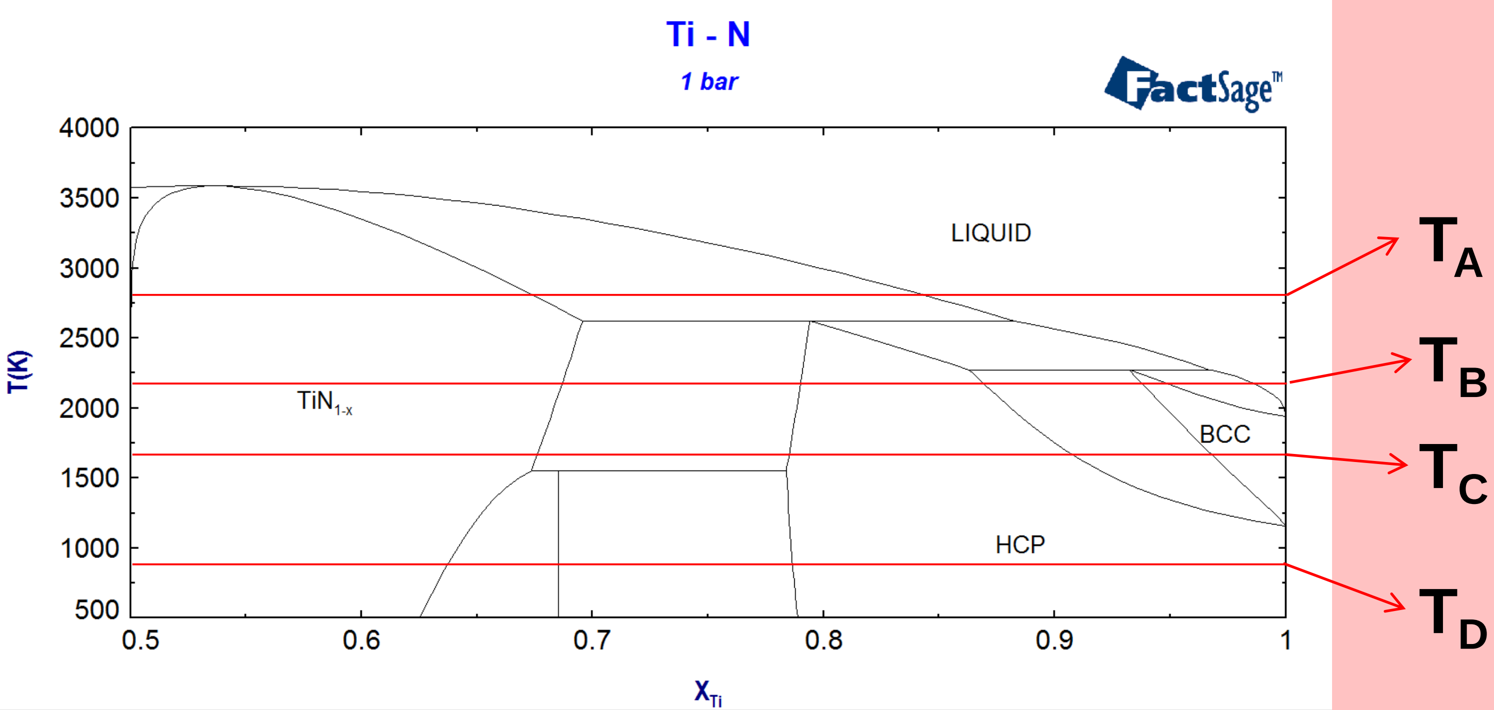
You are interested to learn something about thermodynamics of your material system during BSc/MSc/PhD thesis / at work: What do you do?

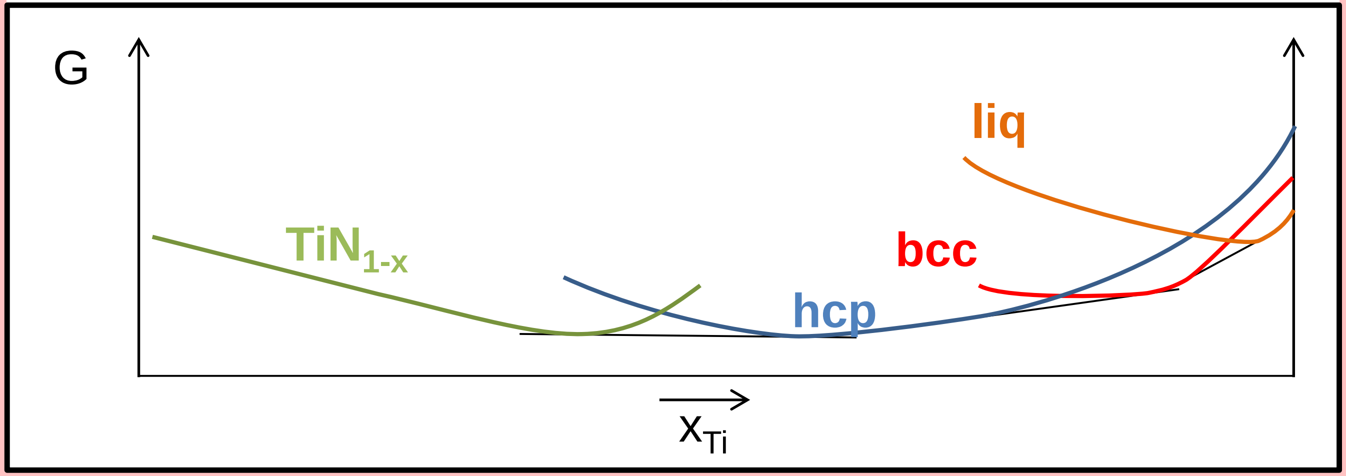
→ CHECK PHASE DIAGRAMS E.G. AT

www.springermaterials.com
www.factsage.com
www.asminternational.org/phase-diagrams
www.msiport.com

...

At what temperature do you expect G(x) curves as shown?





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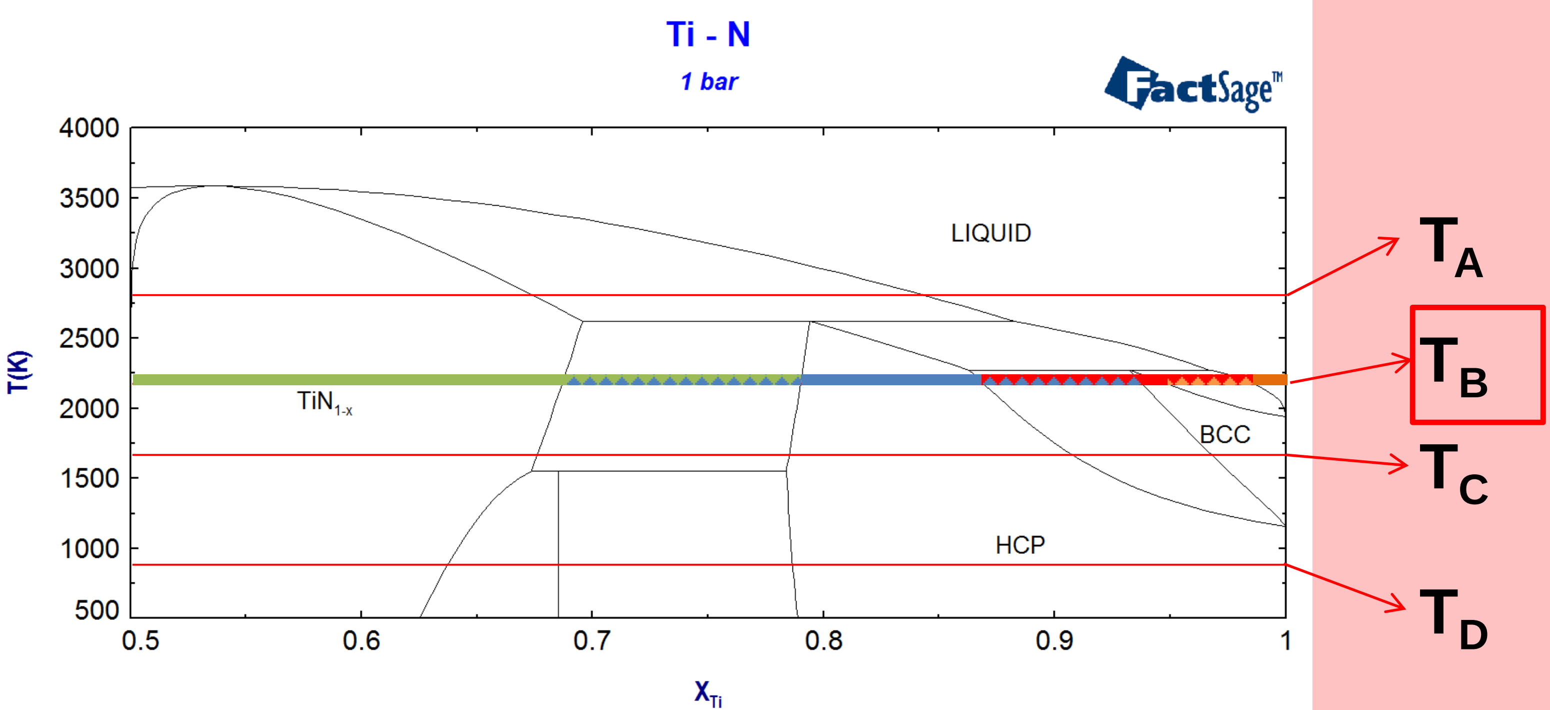
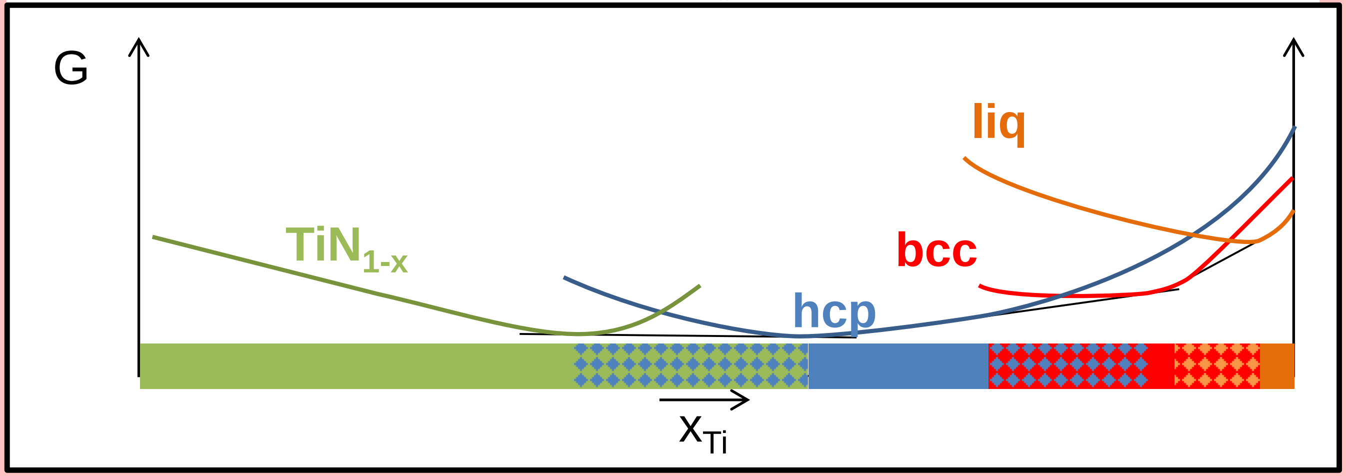




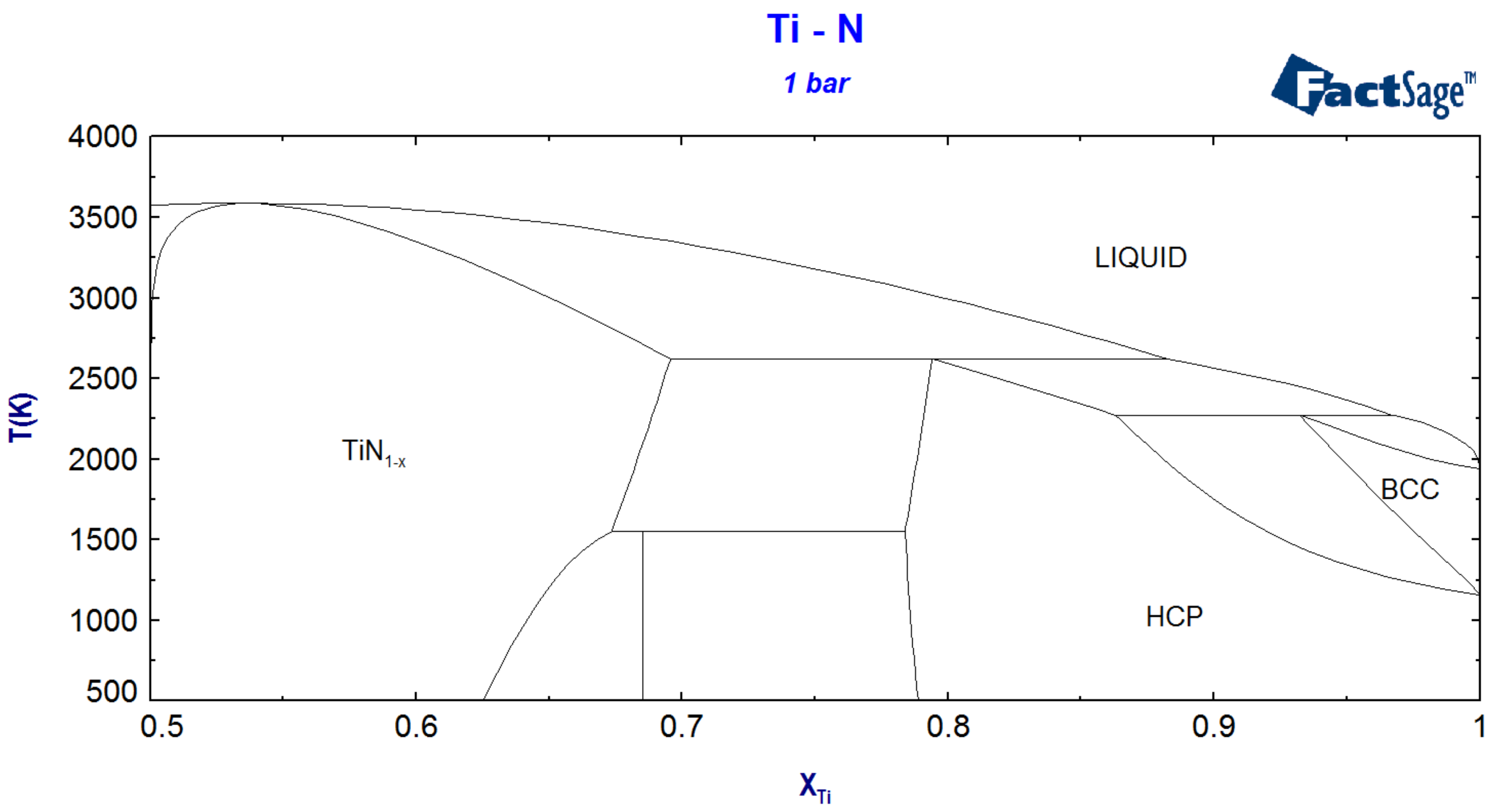
What information can you extract concerning Ω?

A: $\Omega_{Ti\text{-}N} << 0$

B: $\Omega_{Ti\text{-}N} < 0$

C: $\Omega_{Ti\text{-}N} > 0$

D: $\Omega_{Ti\text{-}N} >> 0$



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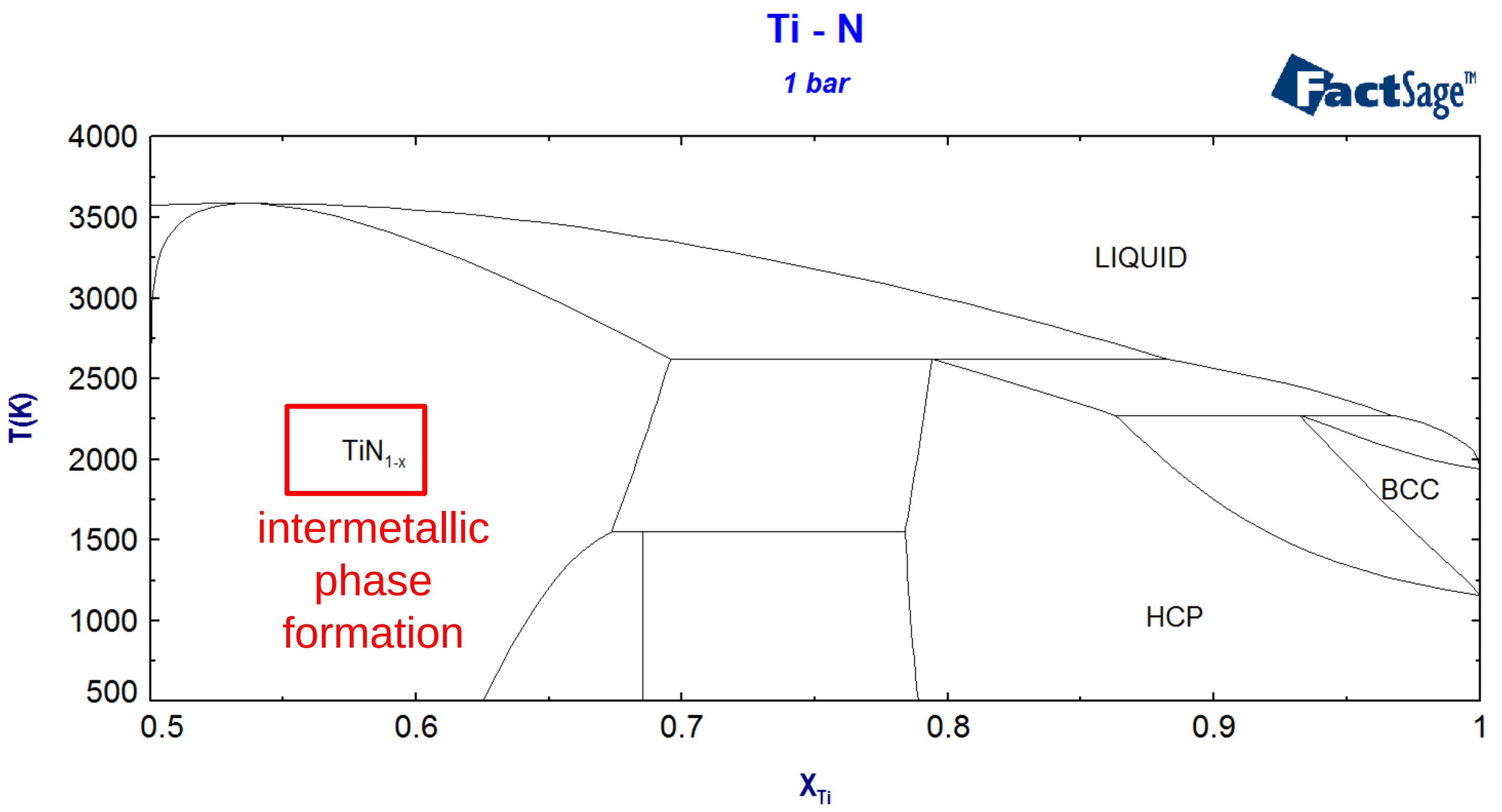
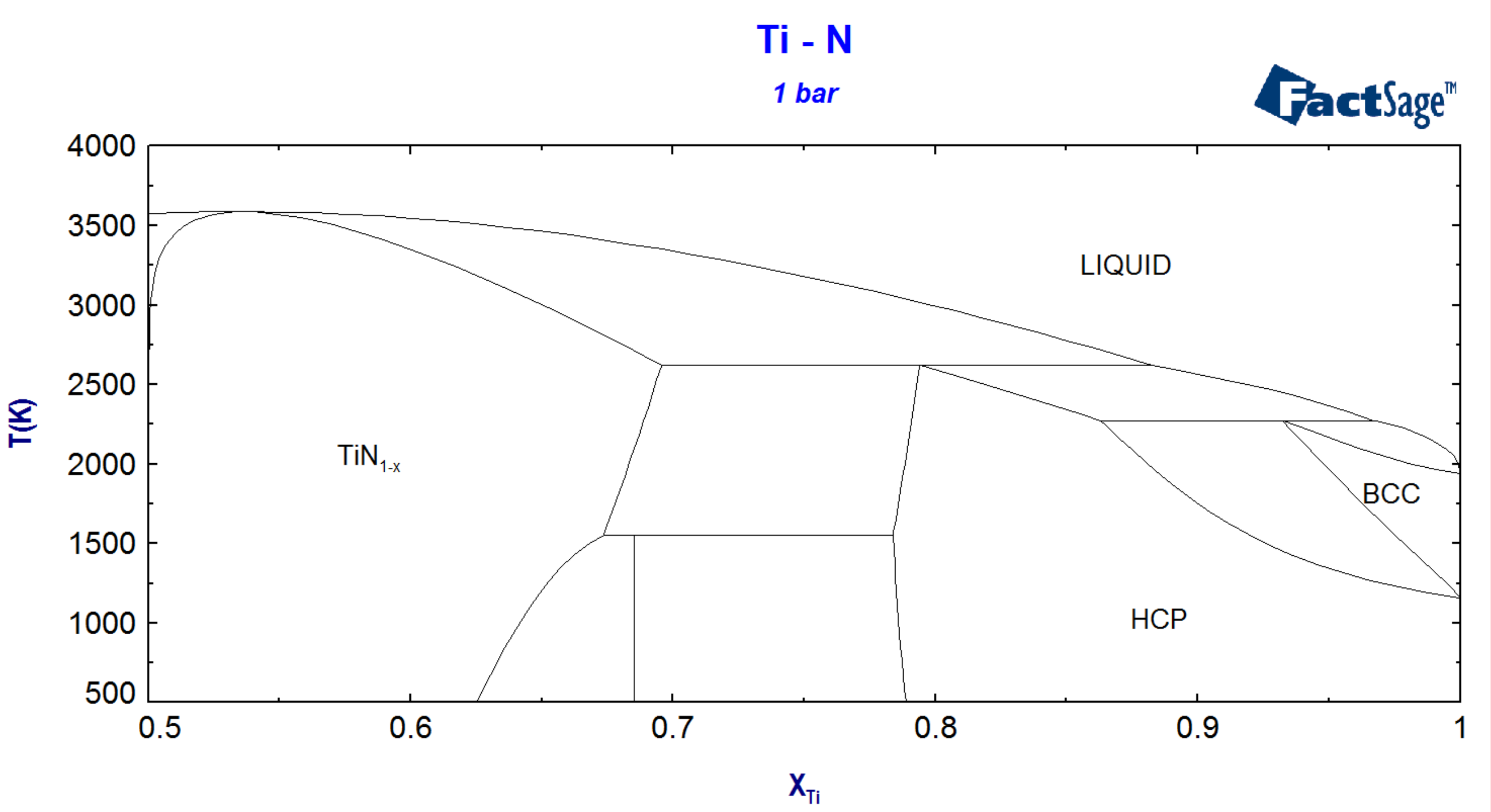


intermetallic phase formation

($\Omega_{Ti\text{-}N} << 0$) What other information can you extract concerning Ω?

A: $\Omega_{Ti\text{-}N,bcc} < \Omega_{Ti\text{-}N,hcp}$

B: $\Omega_{Ti\text{-}N,bcc} > \Omega_{Ti\text{-}N,hcp}$



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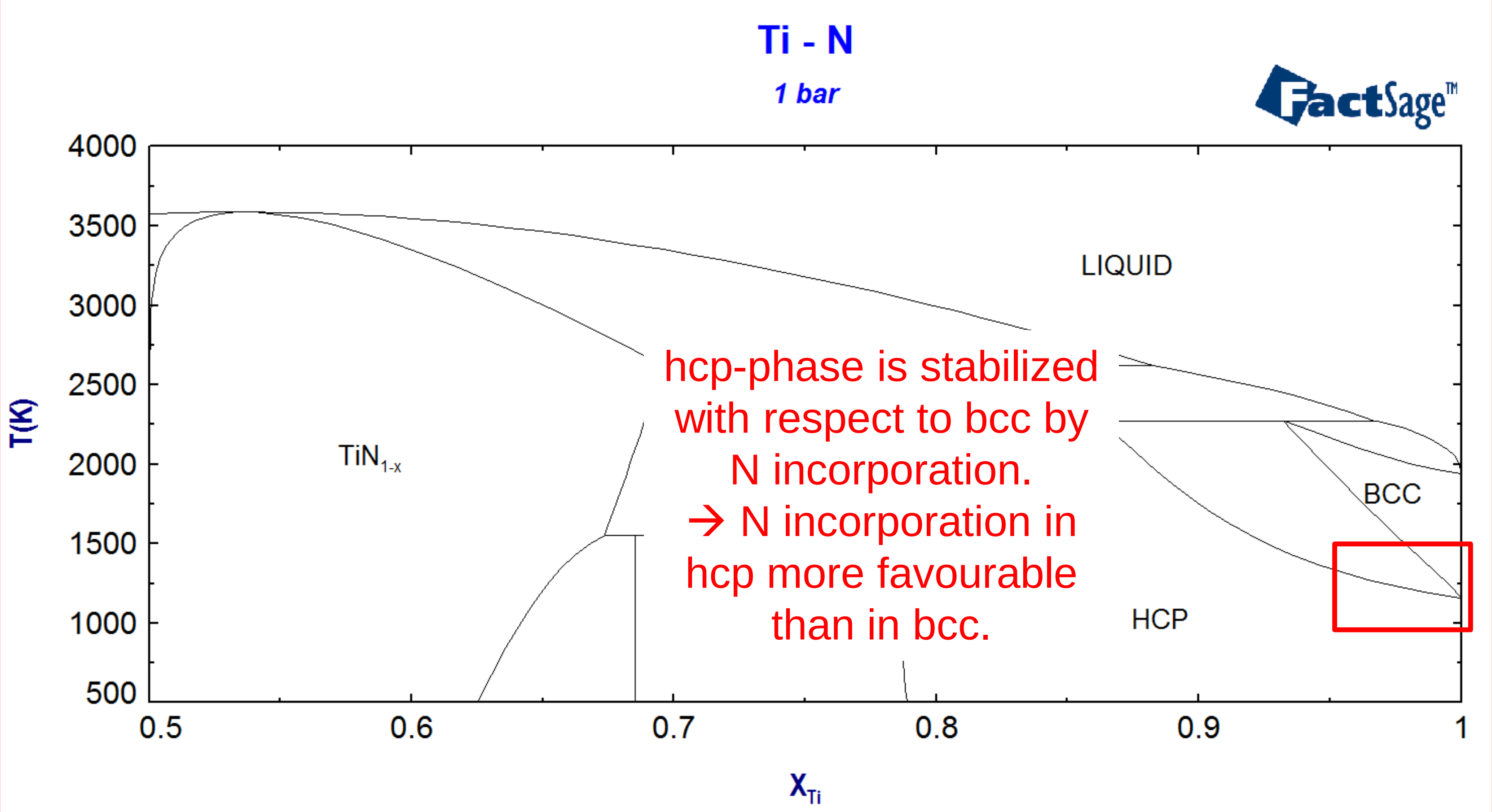
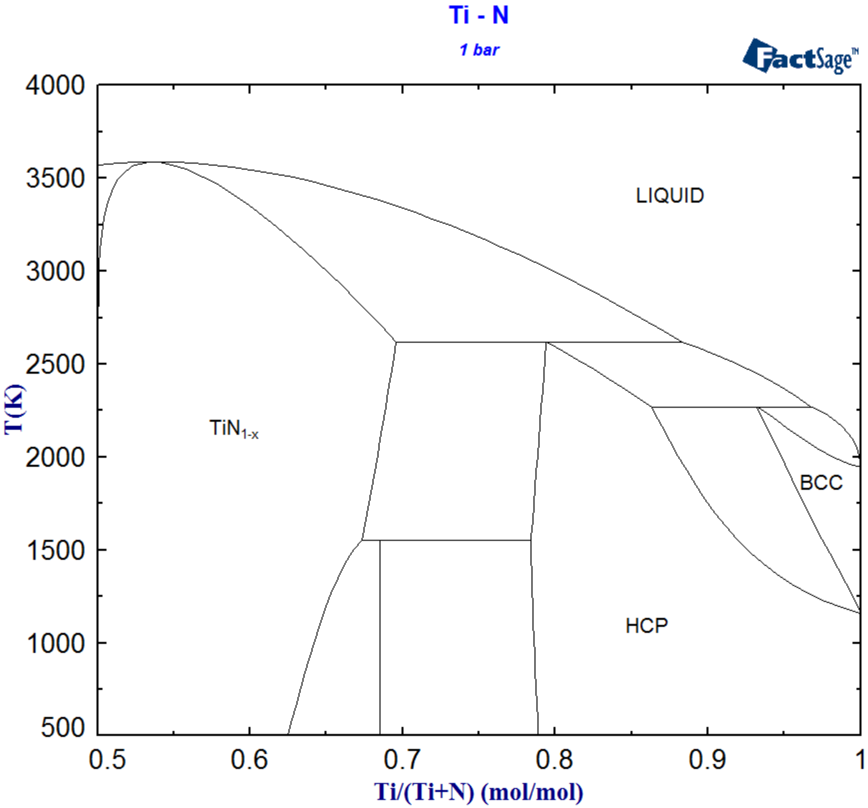
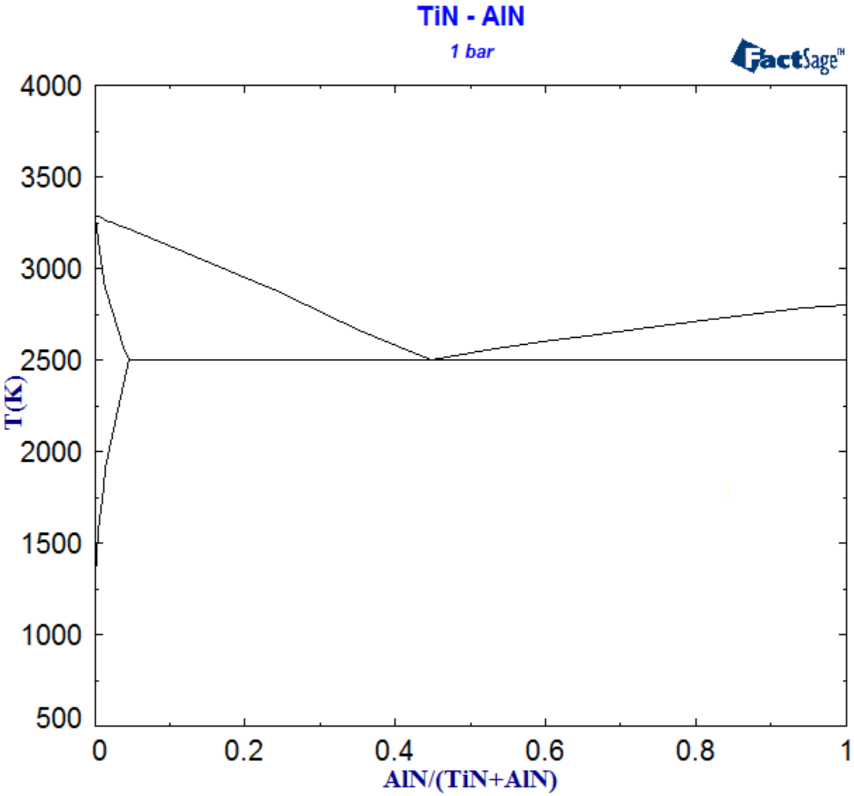


hcp-phase is stabilized with respect to bcc by N incorporation.
→ N incorporation in hcp more favourable than in bcc.

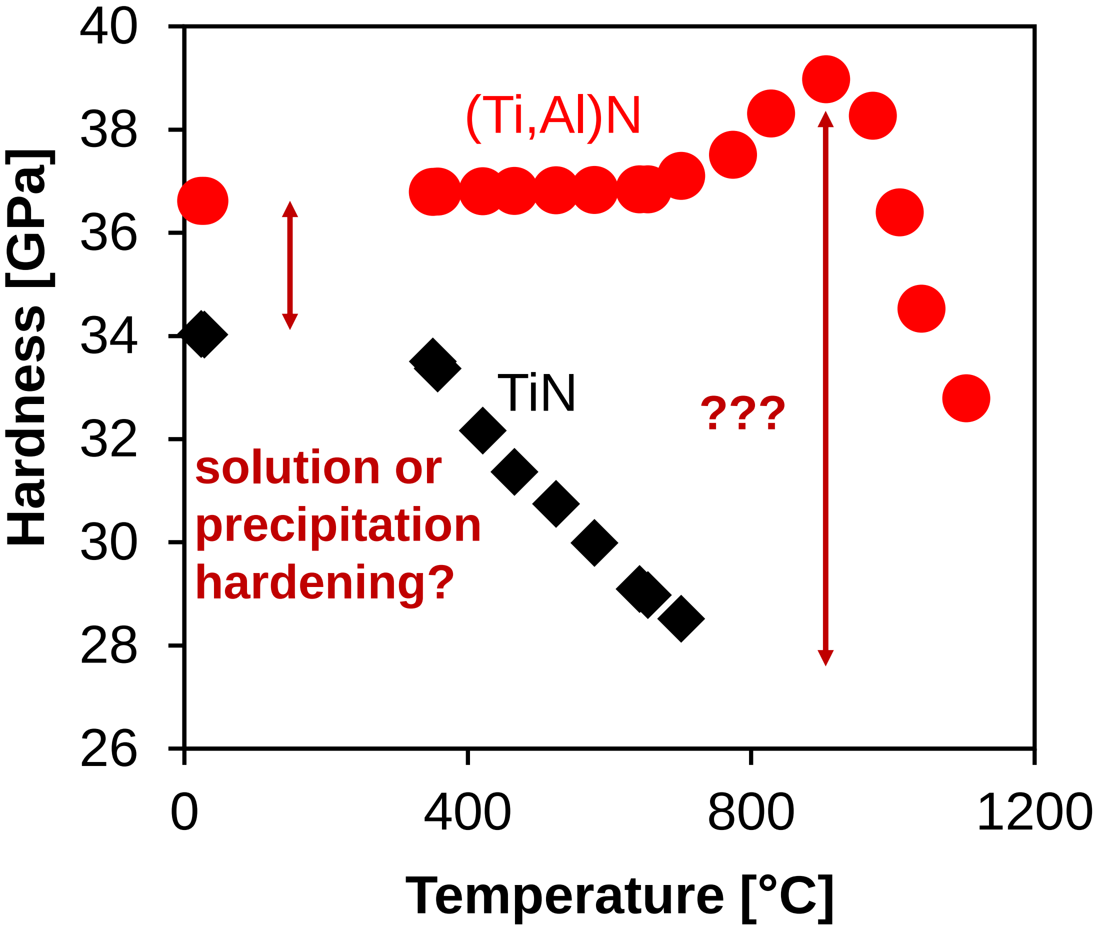
Application: (Ti,Al)N coatings for cutting tools

State of the art for protective coatings on cutting tools :
1980 - 2000 TiN
Since ~2000 (Ti,Al)N coatings WHY?





Application: (Ti,Al)N coatings for cutting tools

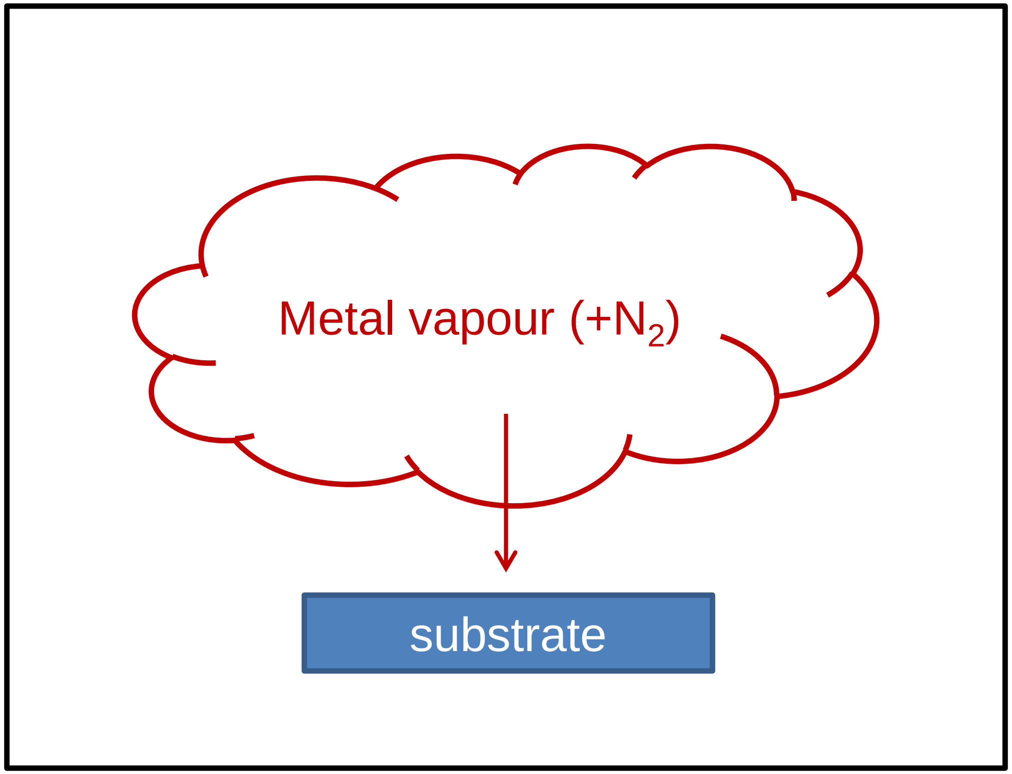


H increases by Al addition!

But WHY?

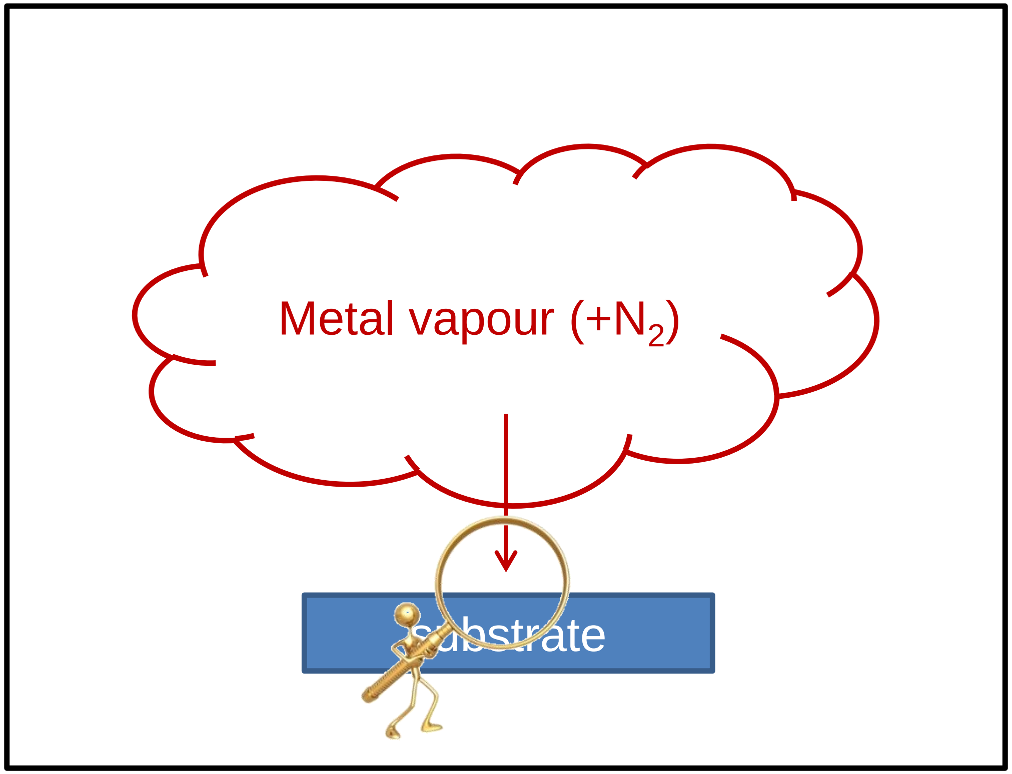
Mayrhofer, Rachbauer, Rovere, Schneider, *Protective Transition Metal Nitride Coatings* (2012).

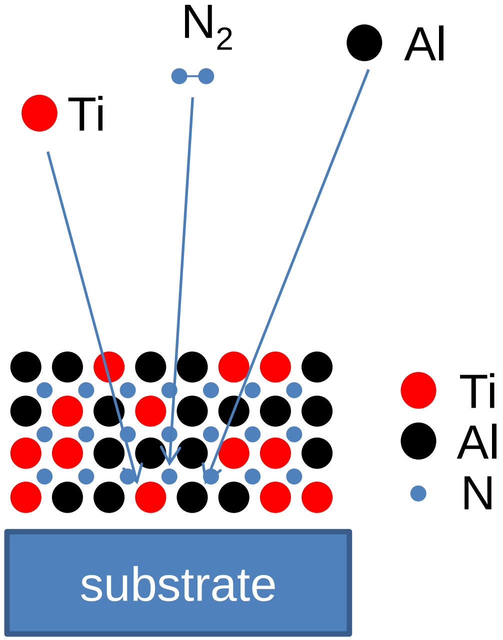
Vapour phase condensation



From metal vapour to solid within a fraction of 1 µs
→ Extreme quenching rates (>> 10^{10} °C/s)!

Vapour phase condensation





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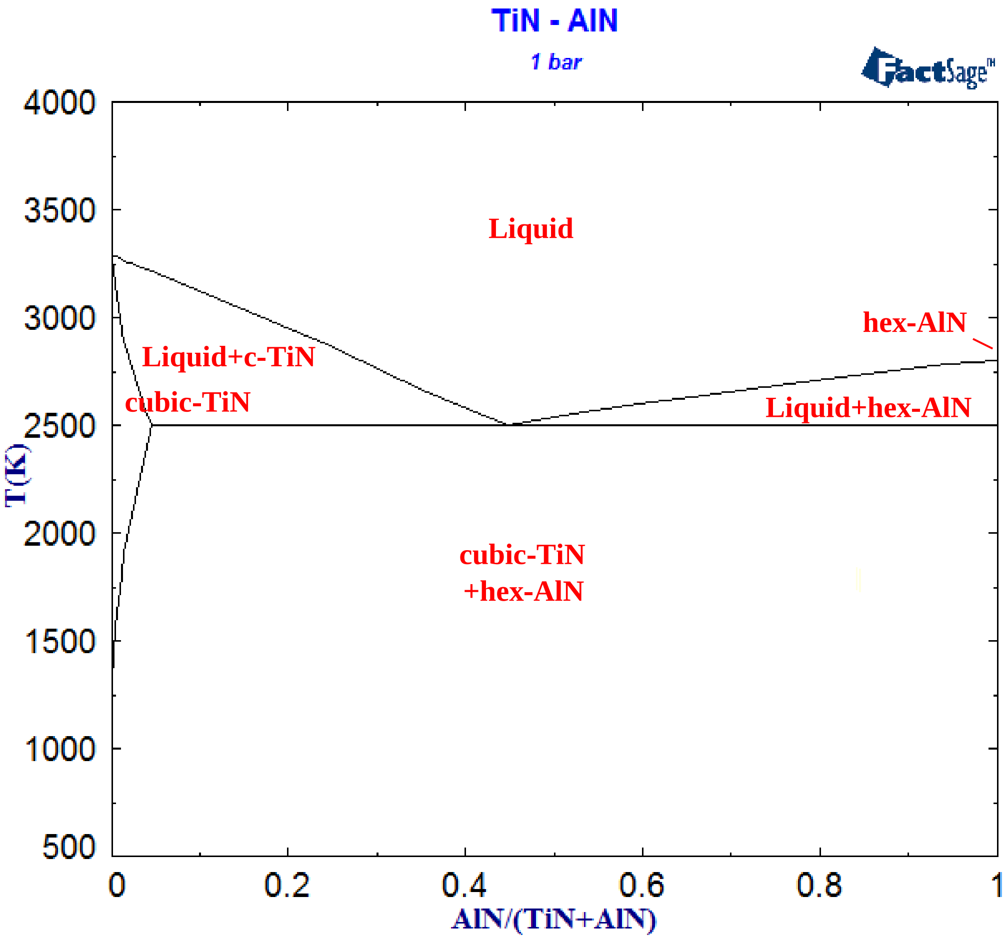
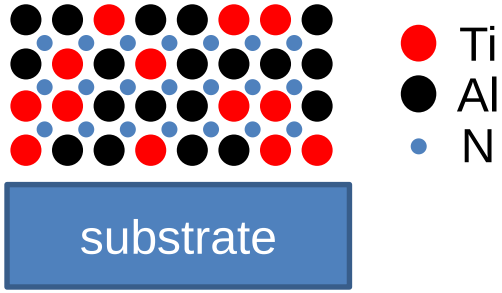


Atoms cannot form two phases TiN+AlN because of limited mobility (non-equilibrium processing).
What do we learn from the phase diagram?
NOTHING AT ALL!?
Wait: Please sketch the G(x) curves at T = 250°C.



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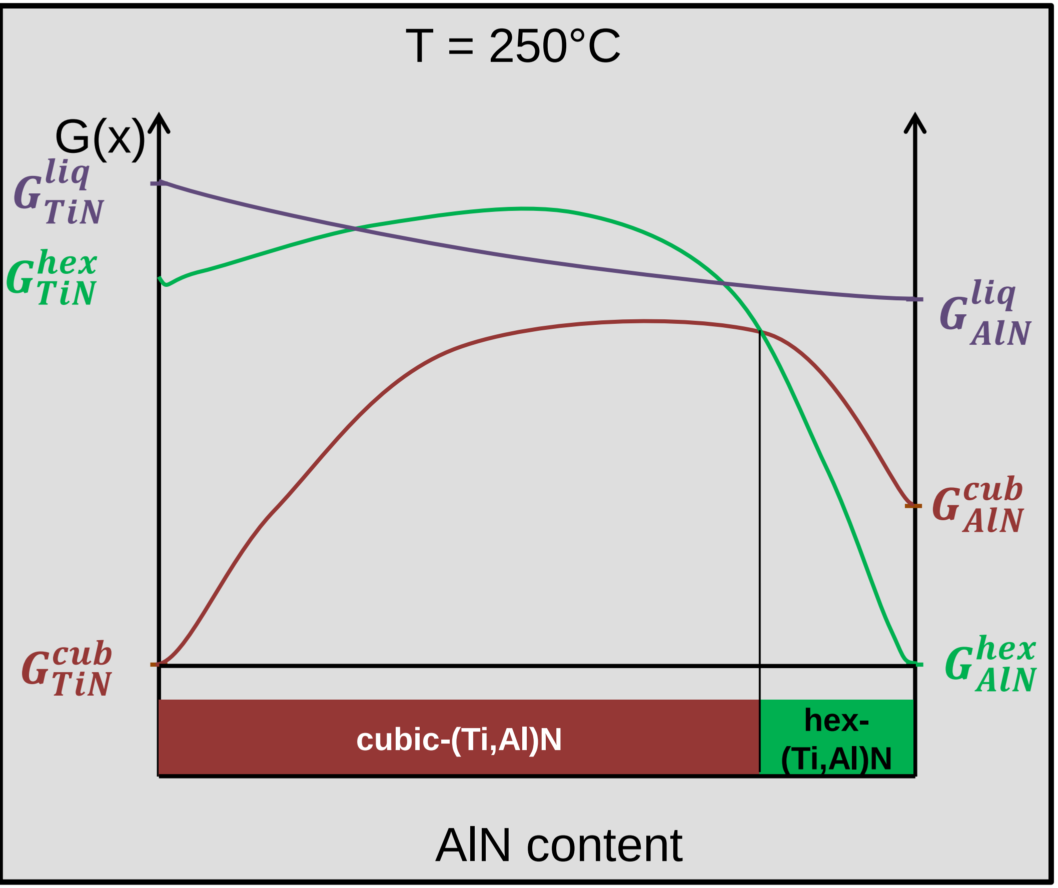
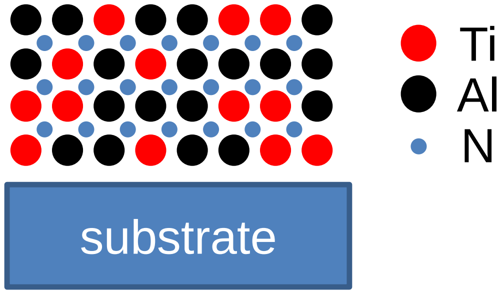


Atoms cannot form two phases TiN+AlN because of limited mobility (non-equilibrium processing).

Therfore, only a single (Ti,Al)N phase can form.

→ What is the single phase with lowest energy?



From metal vapour to solid within a fraction of 1 µs

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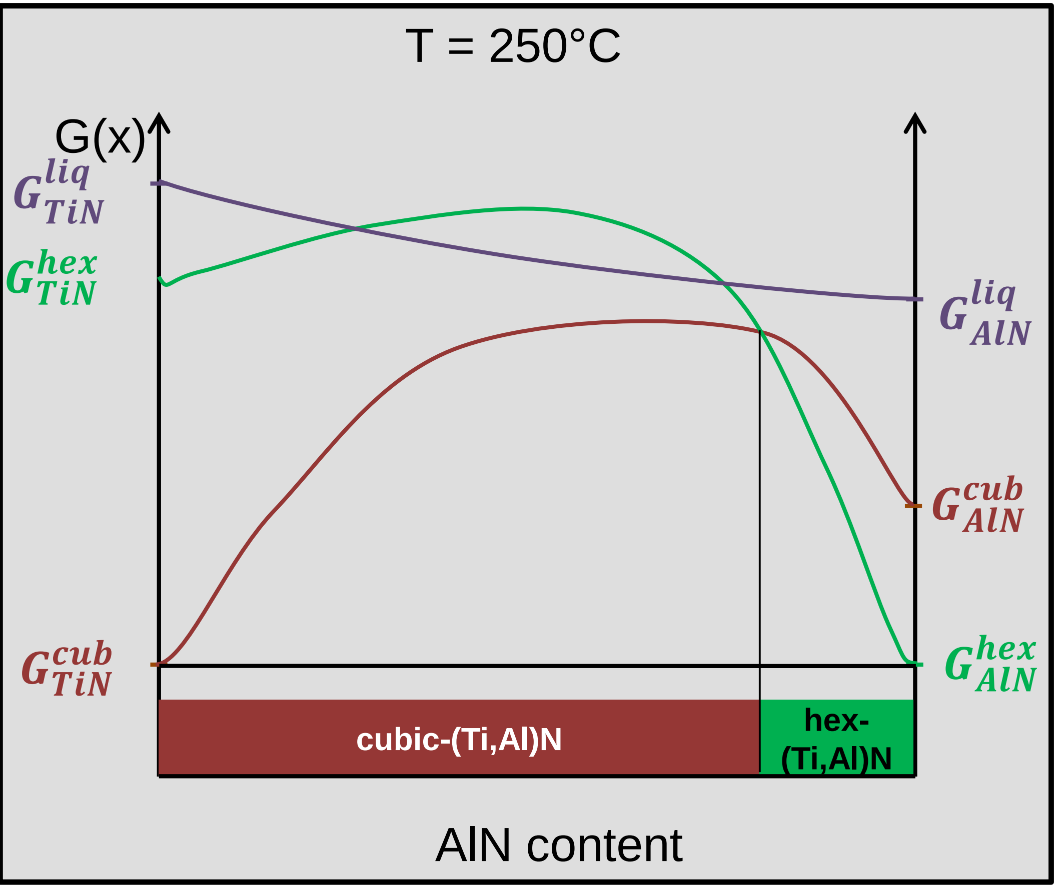
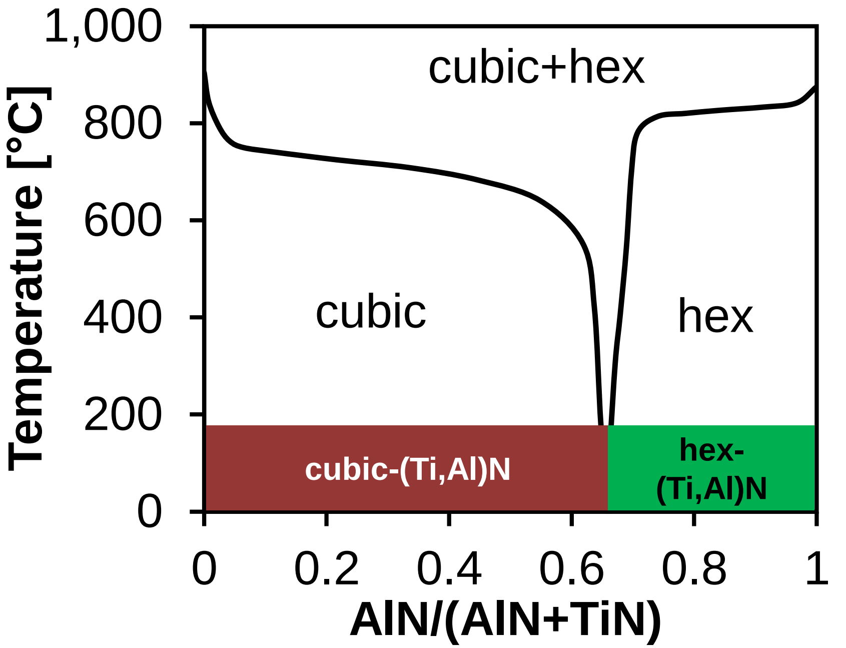
Vapour phase condensation





Experimental non-equilibrium (metastable) TiN-AlN phase diagram [Spencer, Z. Metallk. 92 (2001) 10]

→ G(x) curves can predict metastable phase formation!

From metal vapour to solid within a fraction of 1 µs

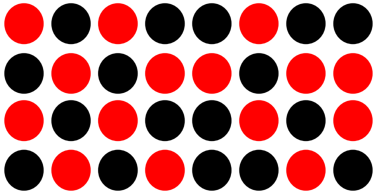
→ Extreme quenching rates (>> 10^{10} °C/s)!

$Ti_{0.5}Al_{0.5}N$: A real solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Think about bonds & configurations

REAL SOLUTIONS

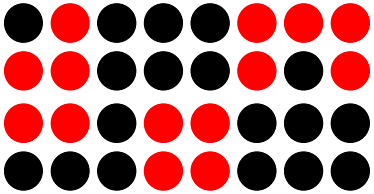


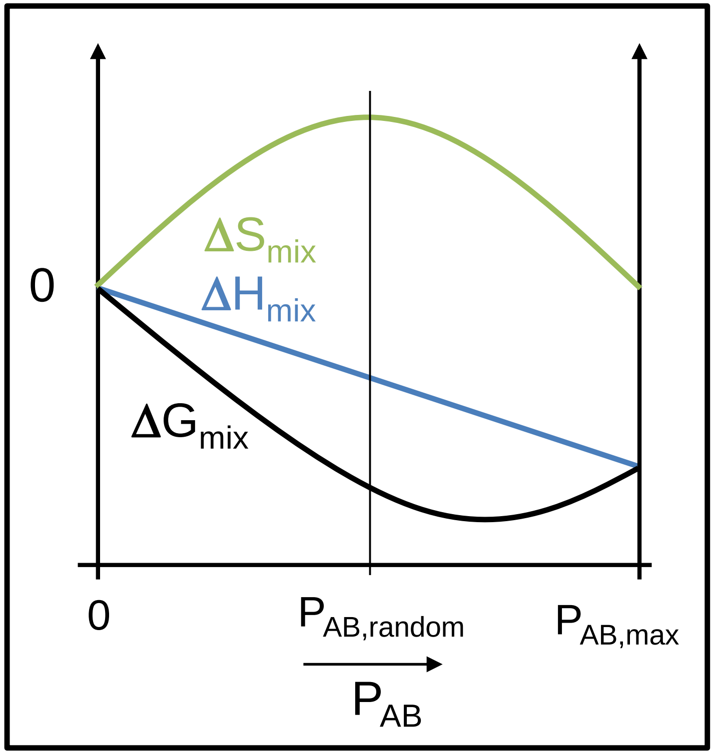
Ω<0

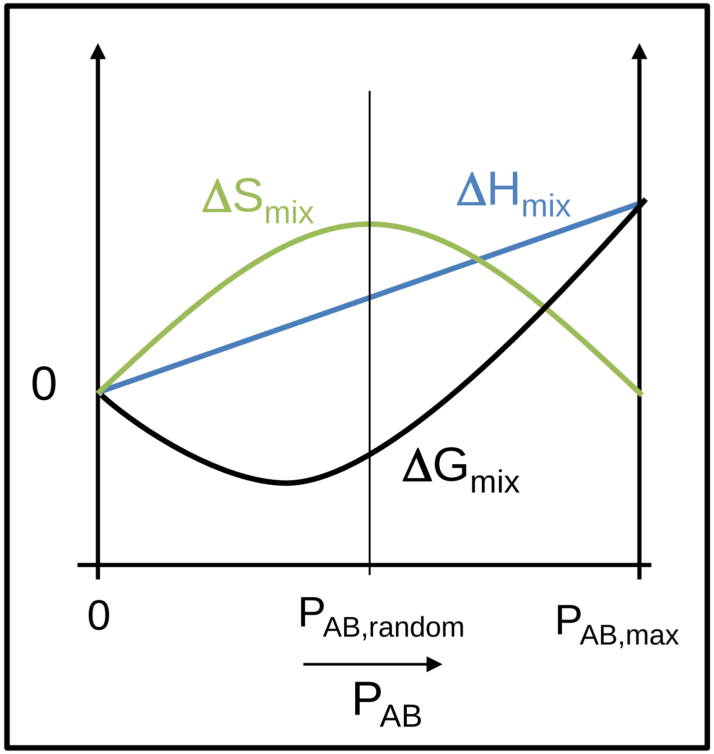
Ordering

Ω>0

Clustering





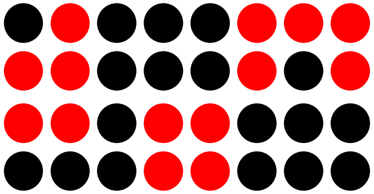


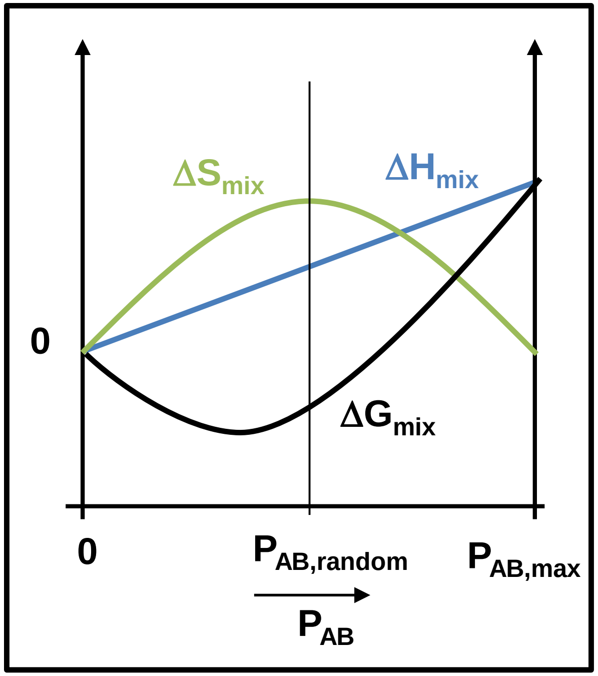
$Ti_{0.5}Al_{0.5}N$: A real solution

Visualizing atomic composition in 3D: 3D atom probe tomography

REAL SOLUTIONS

↓Clustering↓





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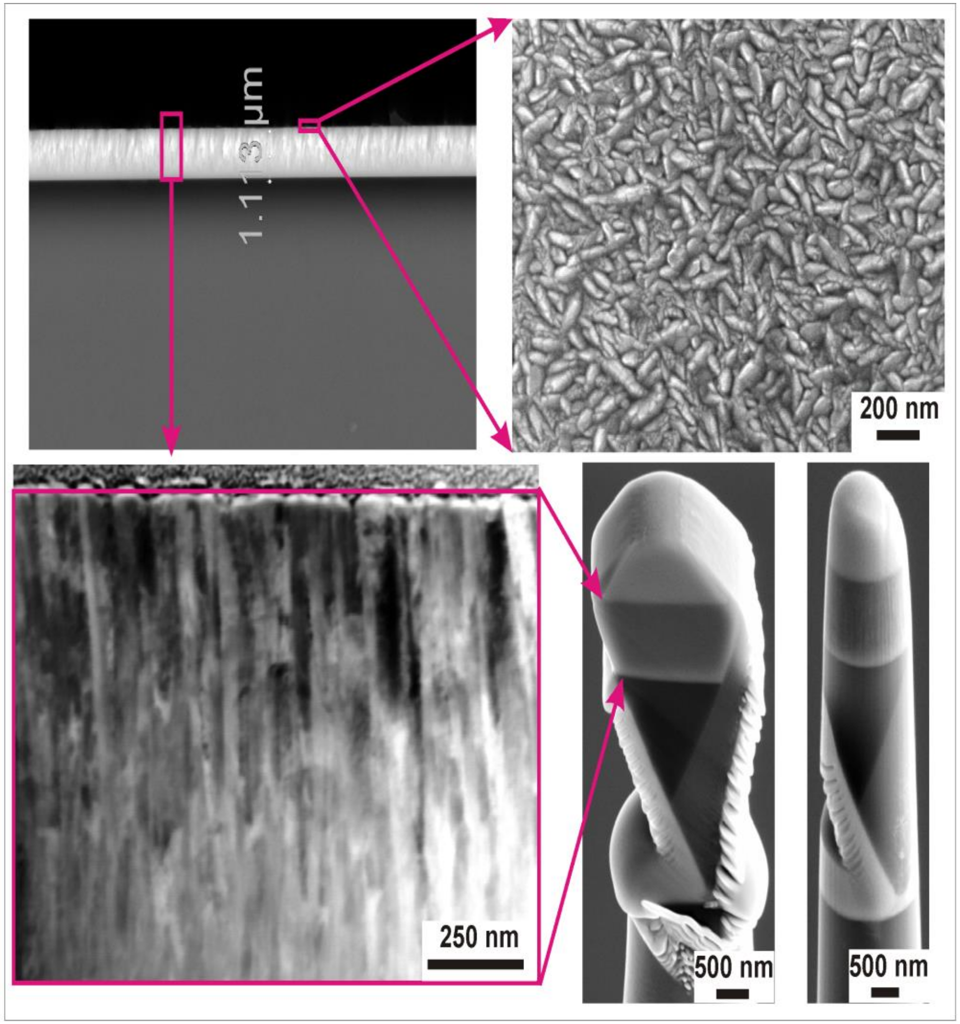
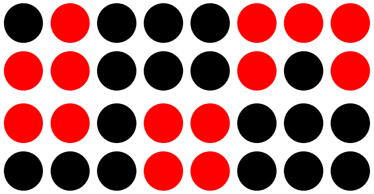
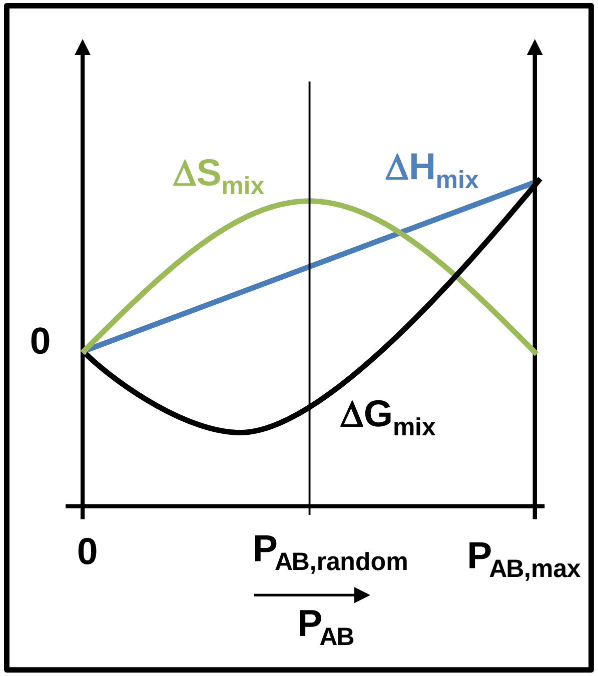


REAL SOLUTIONS

↓Clustering↓





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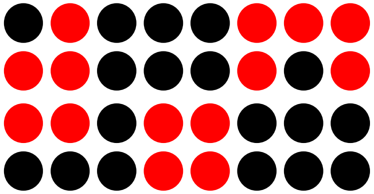

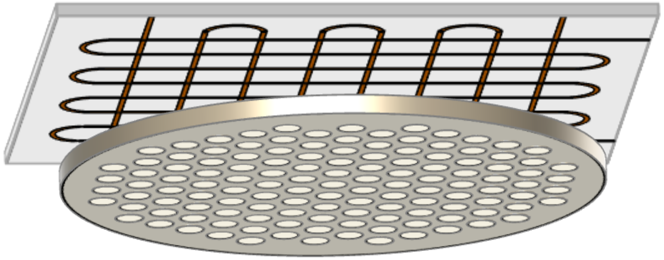

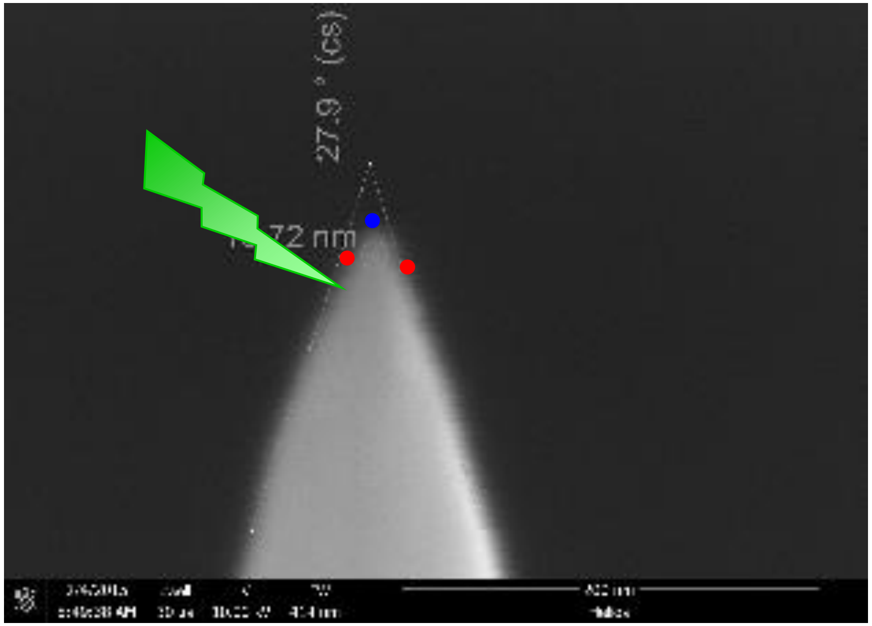

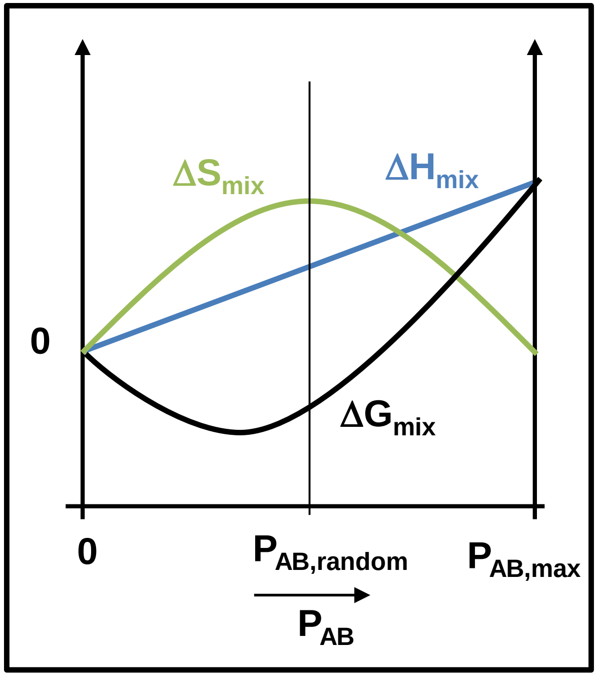

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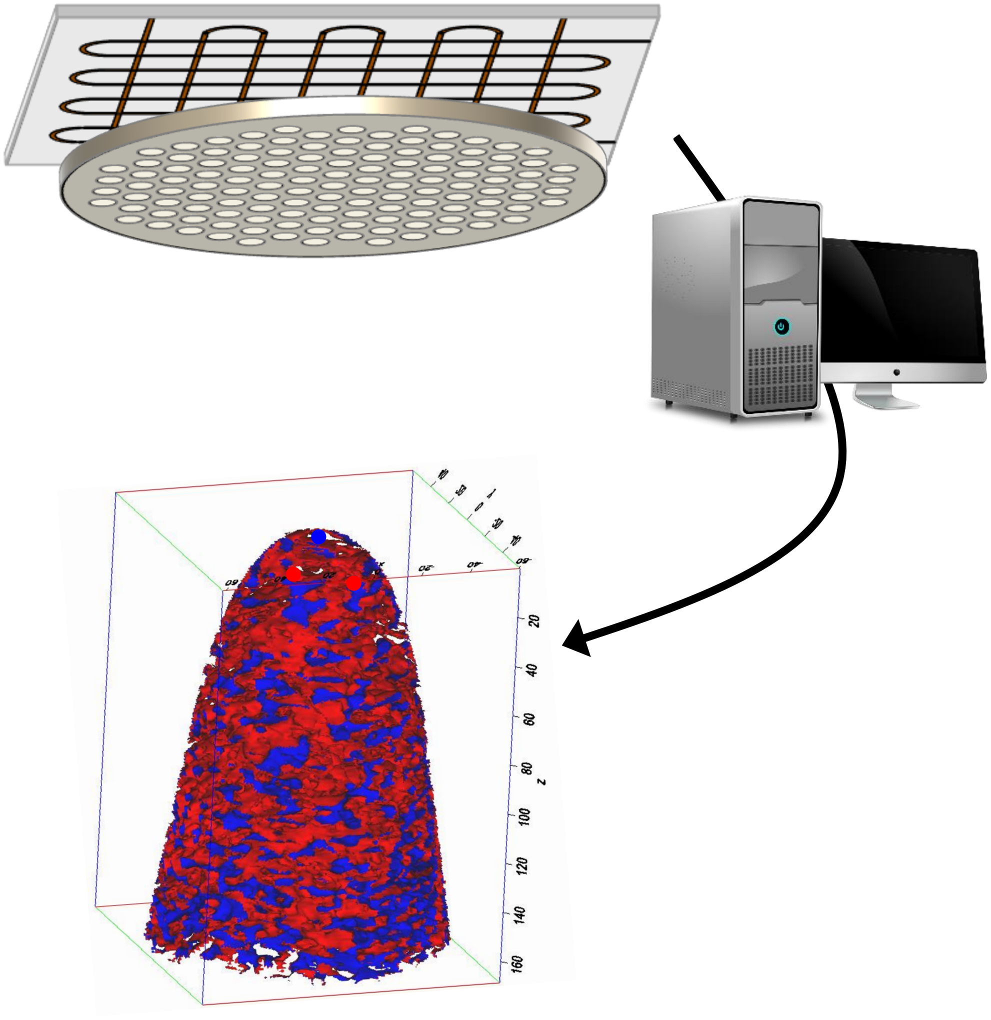

REAL SOLUTIONS

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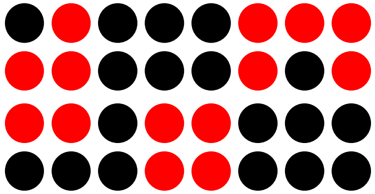

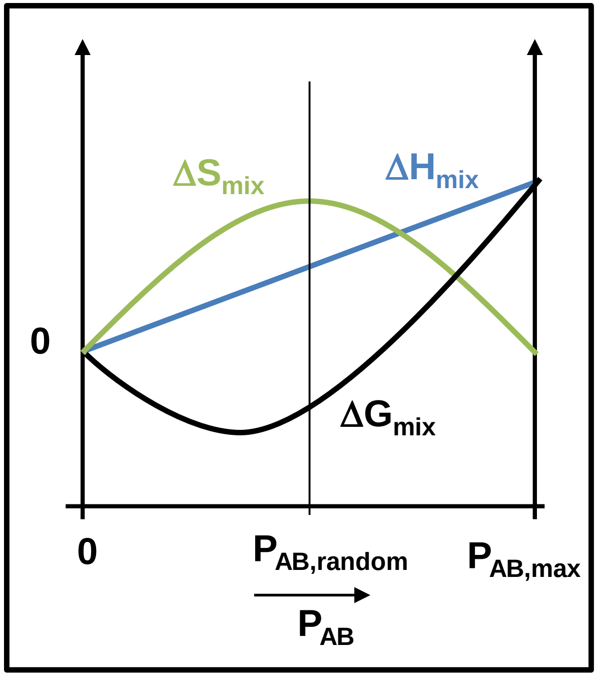

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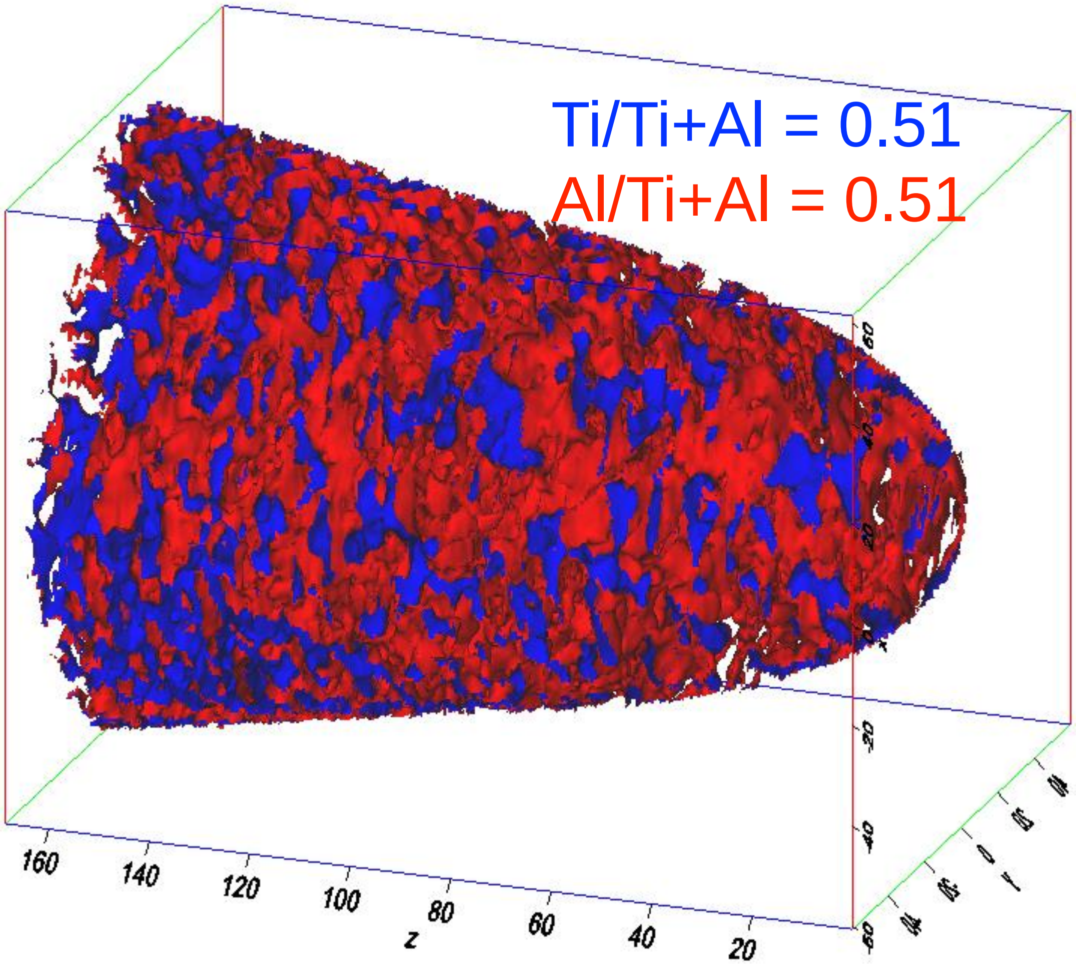
Visualizing atomic composition in 3D: 3D atom probe tomography

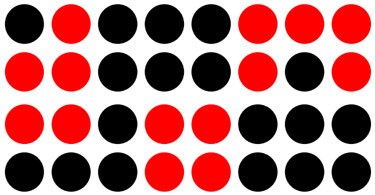


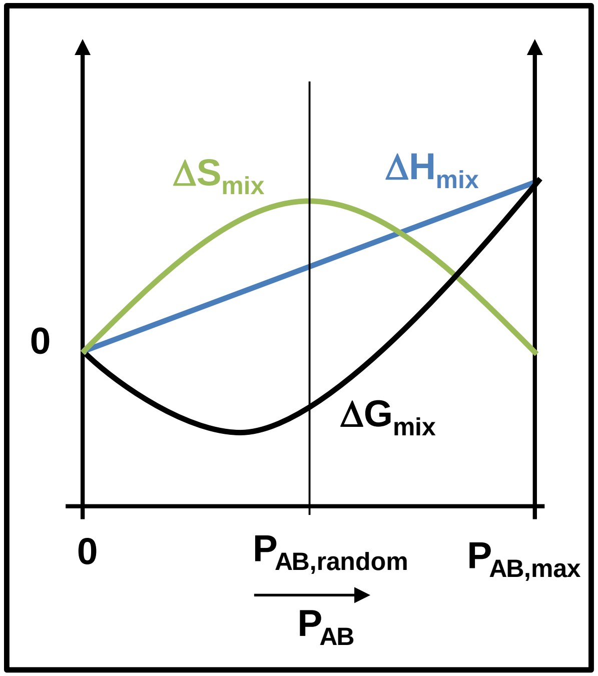
Ti/Ti+Al = 0.51

Al/Ti+Al = 0.51

REAL SOLUTIONS

↓Clustering↓





Concepts, key ideas

Strategy for predicting metastable phase formation in vapour phase condensation:

1. Derive G(x) curves from the stable phase diagram.
2. For each composition, the single phase with lowest Gibbs energy forms during vapour phase condensation.

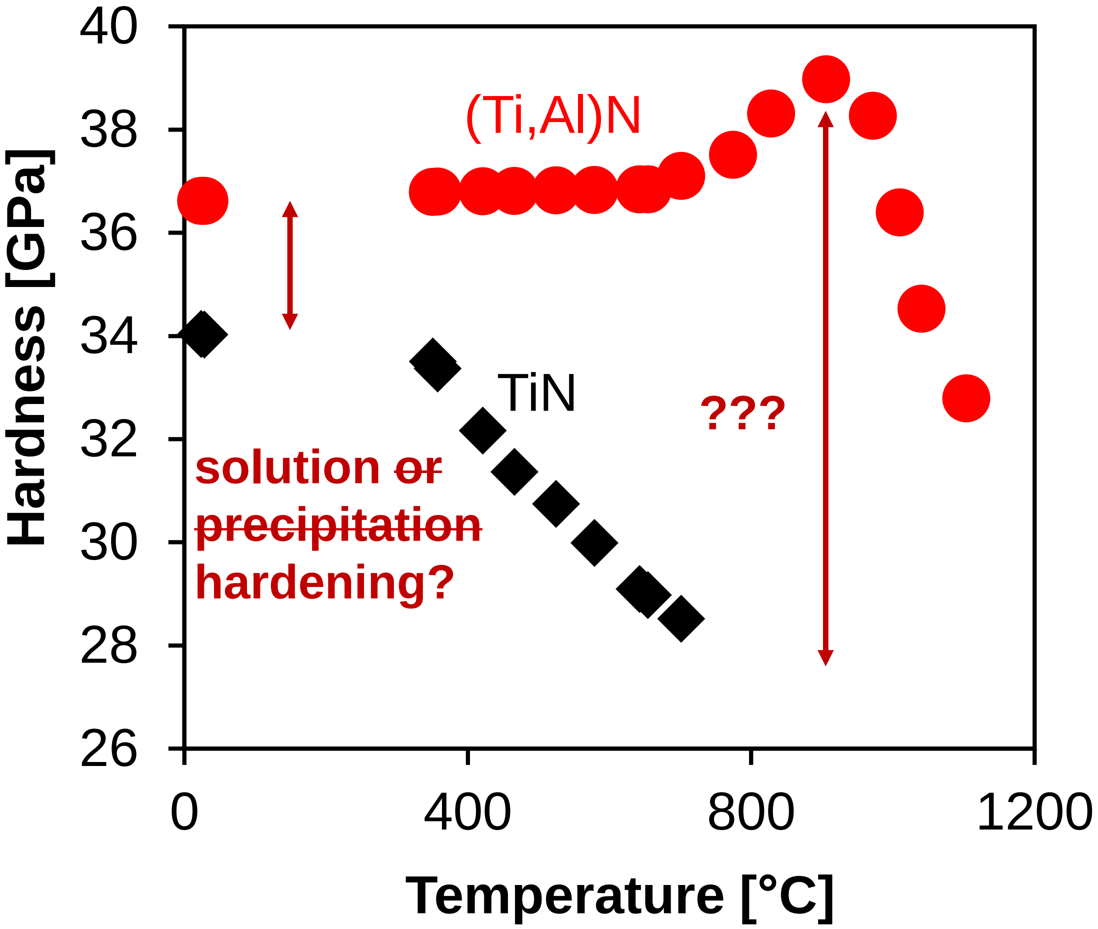
In real solutions, atoms form short-range order to minimize G:

clustering in case of $\Omega > 0$ or

ordering in case of $\Omega < 0$.

This ordering can be observed!

Application: (Ti,Al)N coatings for cutting tools



solution ~~or~~ ~~precipitation~~ hardening?

???

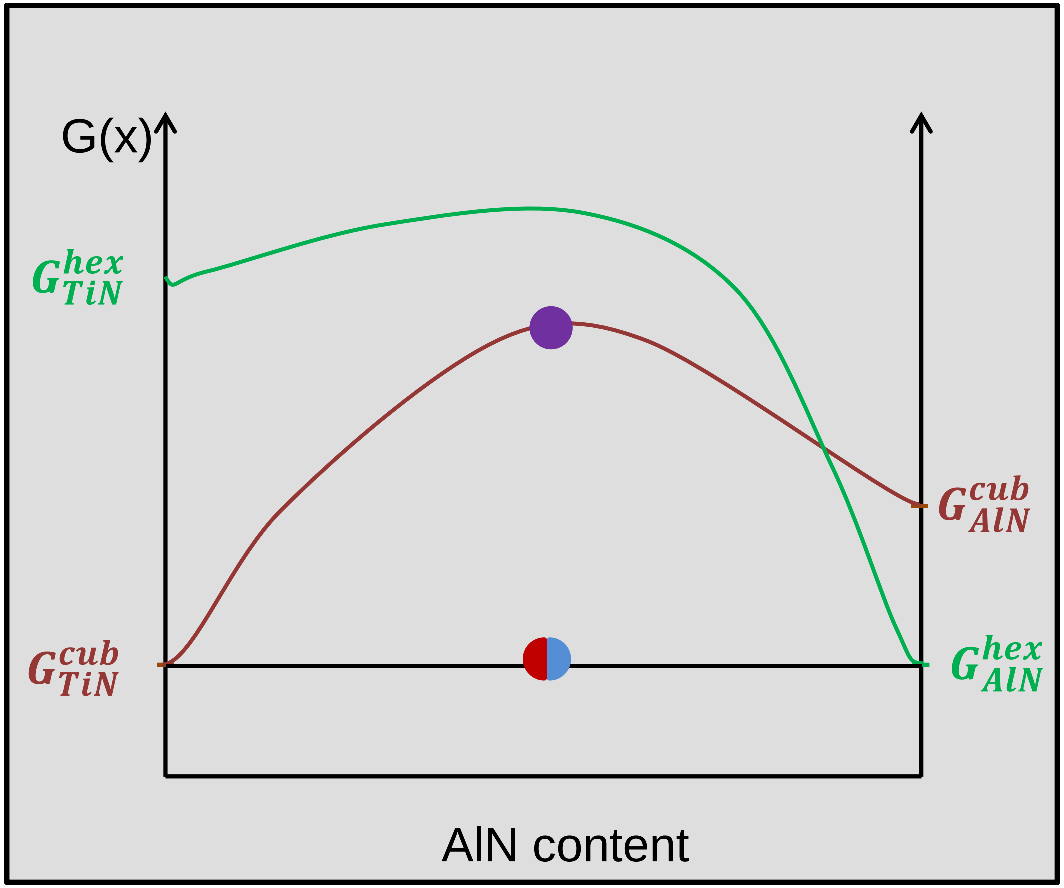
H increases by Al addition!

But WHY?

Let‘s look at G(x) curves!

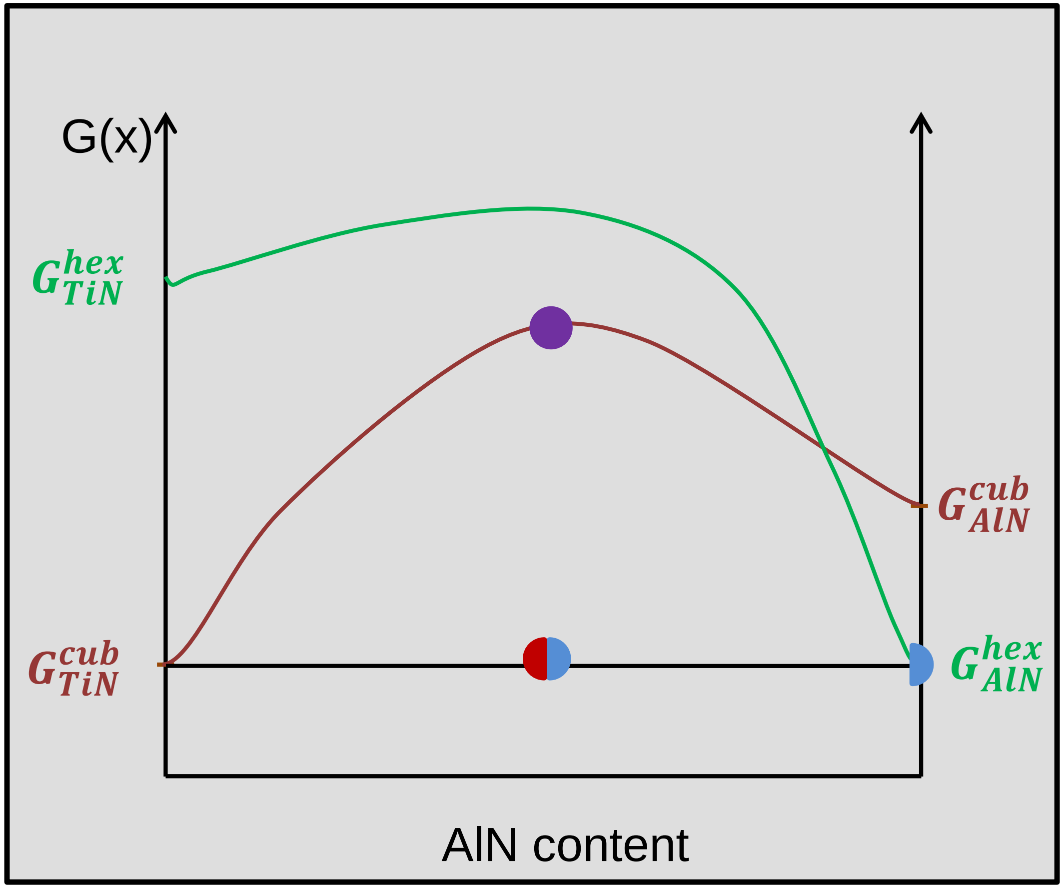
Mayrhofer, Rachbauer, Rovere, Schneider, *Protective Transition Metal Nitride Coatings* (2012).

Annealing of a metastable phase: How can the Gibbs energy be lowered?



1. What is the stable state for $Ti_{0.5}Al_{0.5}N$?
→ cub-TiN + hex-AlN

Annealing of a metastable phase:
How can the Gibbs energy be lowered?



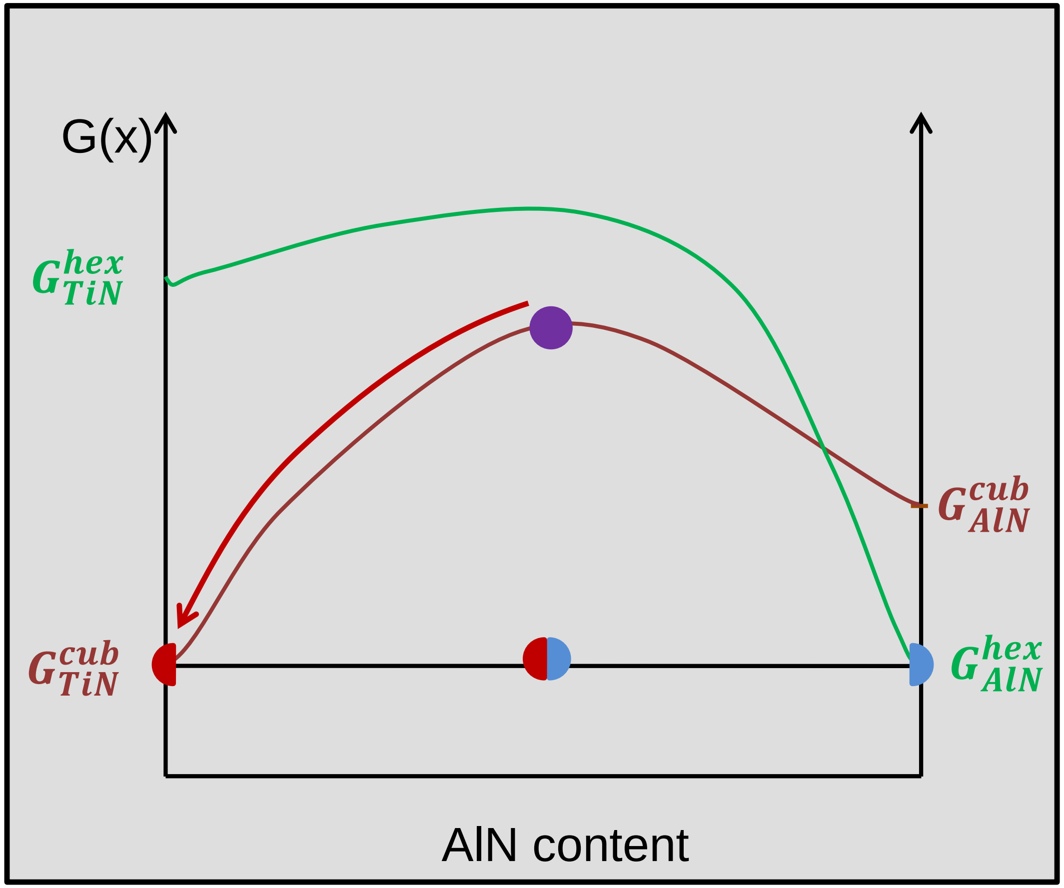
1. What is the stable state for $Ti_{0.5}Al_{0.5}N$?

→ cub-TiN + hex-AlN

2. How can hex-AlN form?

→ Only by precipitation

Annealing of a metastable phase:
How can the Gibbs energy be lowered?



1. What is the stable state for $Ti_{0.5}Al_{0.5}N$?

→ cub-TiN + hex-AlN

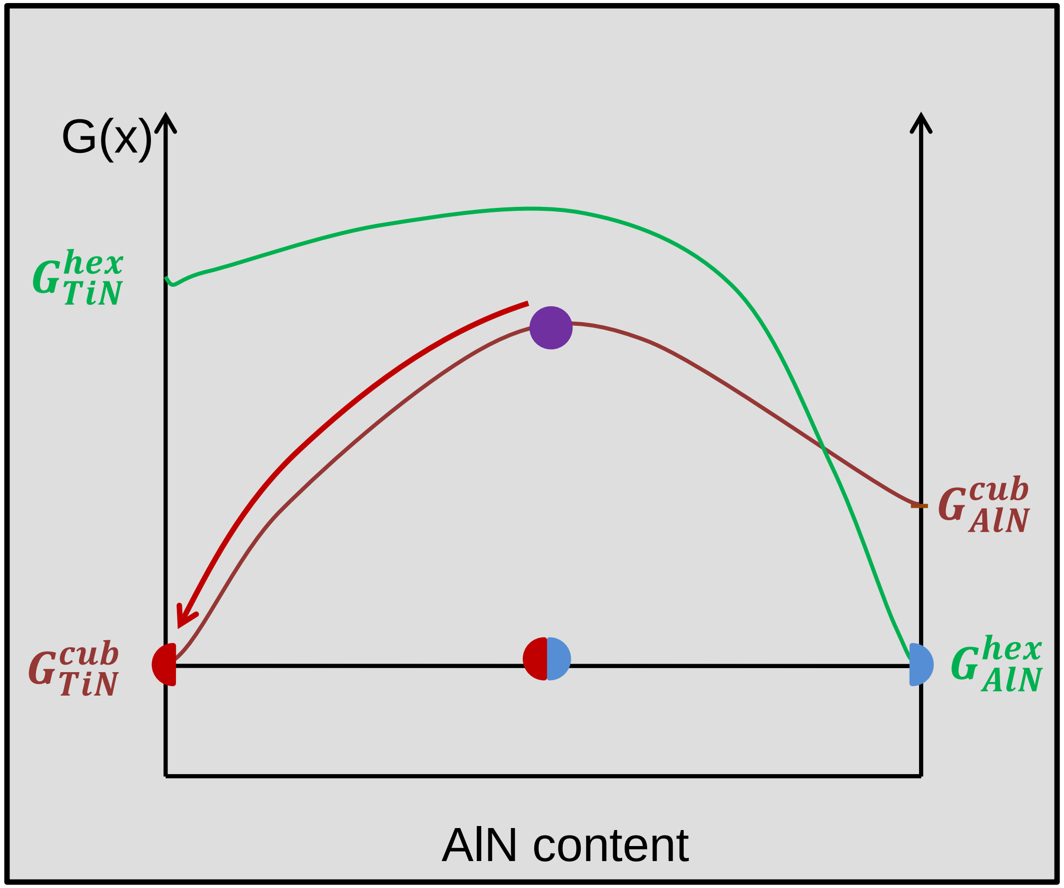
2. How can hex-AlN form?

→ Only by precipitation

3. How can cub-TiN form?

→ Either by de-mixing or by precipitation

Annealing of a metastable phase: How can the Gibbs energy be lowered?



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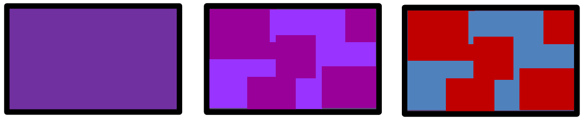
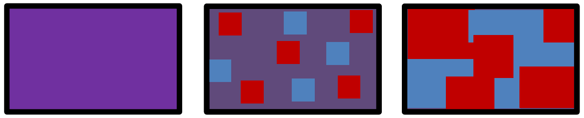
4. What are the activation energies for de-mixing and for precipitation?

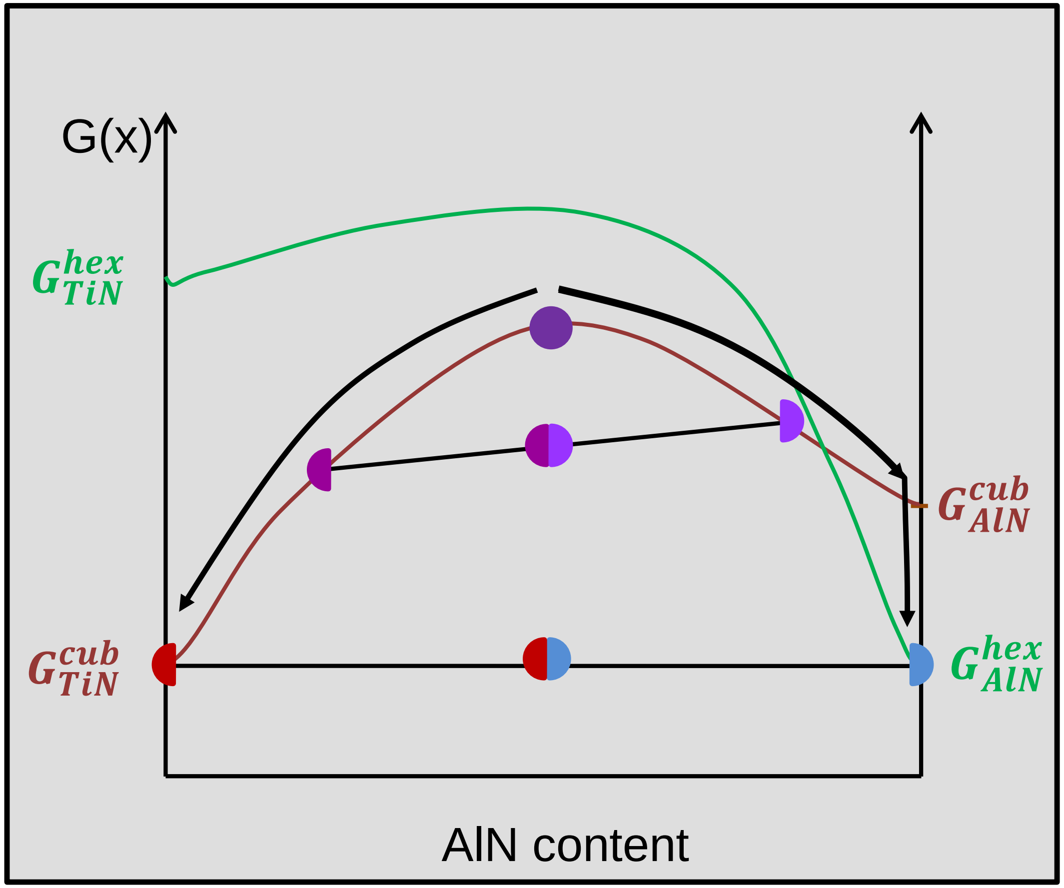


E_A(de-mixing) = E_A(diffusion)



E_A(precipitation) = E_A(nucleation) + E_A(diffusion)

Annealing of a metastable phase: How can the Gibbs energy be lowered?



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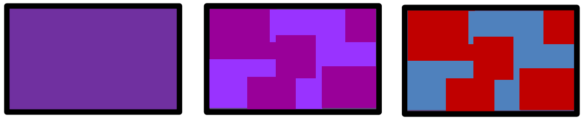

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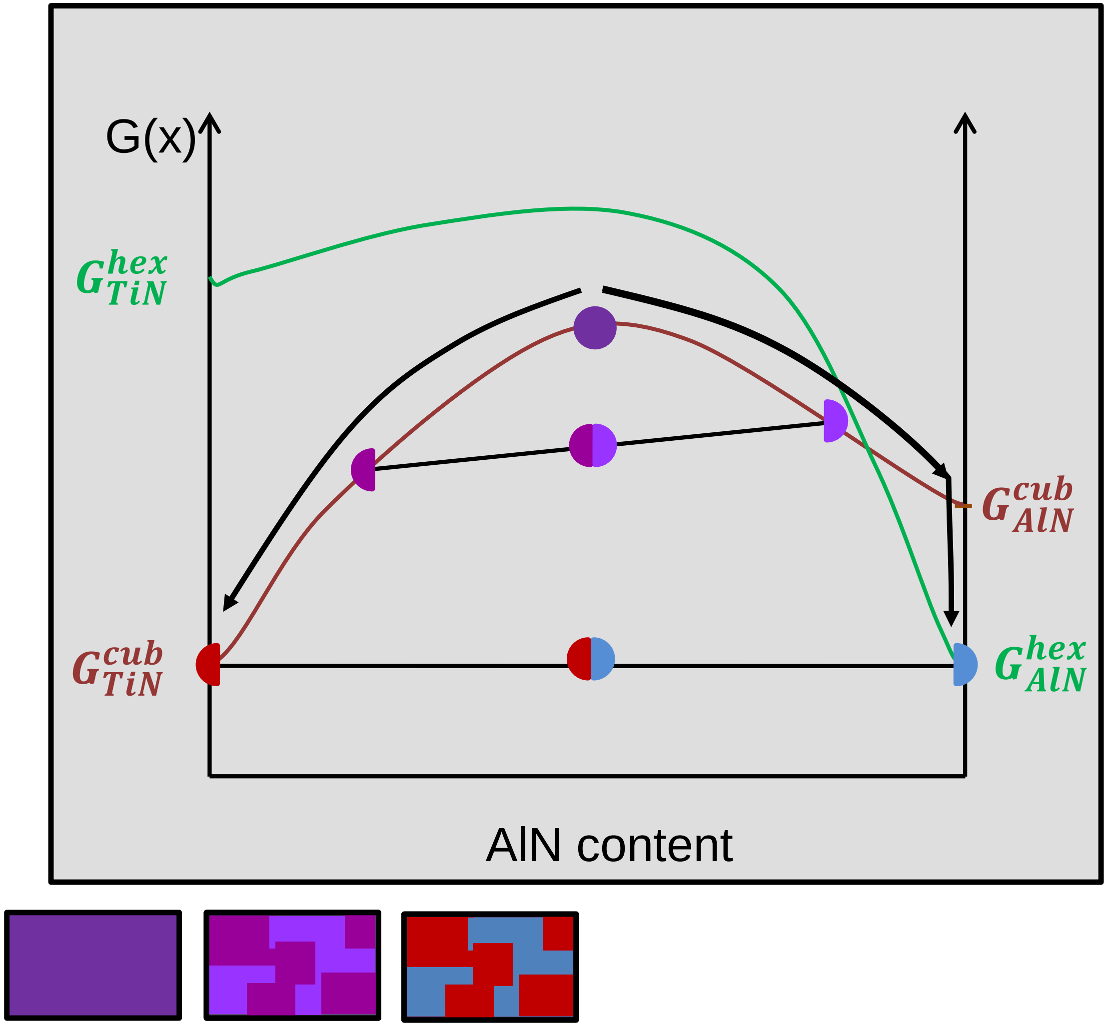
5. Draw intermediate energy steps.

Annealing of a metastable phase: How can the Gibbs energy be lowered?



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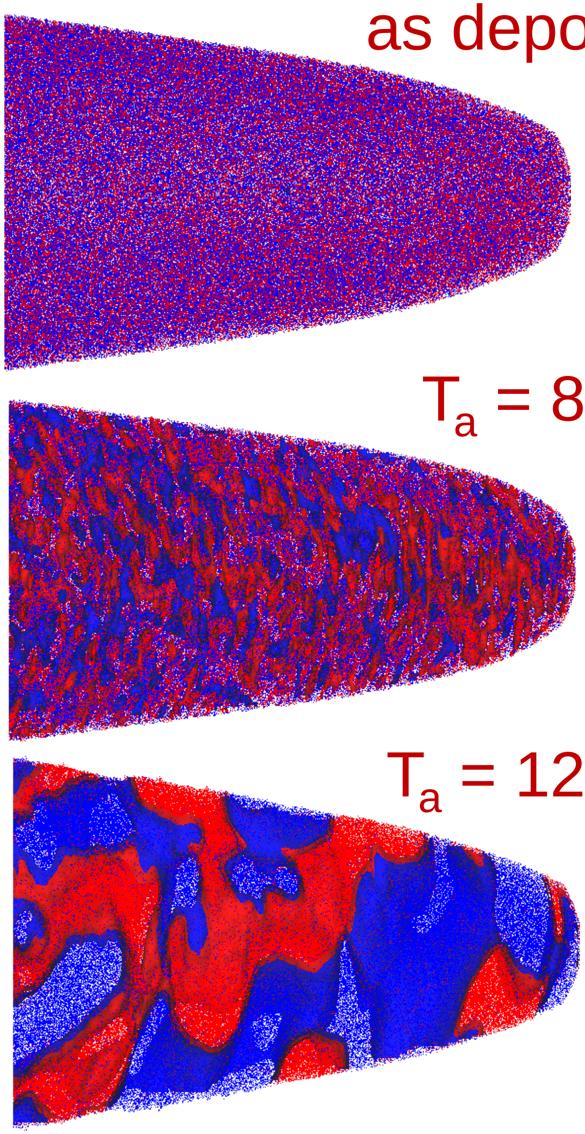

as deposited

T_a = 850°C

T_a = 1200°C

to Baben et al., Materials Research Letters 2016

Thank you for your attention!