FAMSE: Fundamental Aspects of Material Science and Engineering

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Fundamental Aspects of Materials Science and Engineering (FAMSE)

Thermodynamics in materials science, high entropy alloys

Tong Li

Atomic-scale Characterisation

Fundamental Aspects of Materials Science and Engineering (FAMSE)

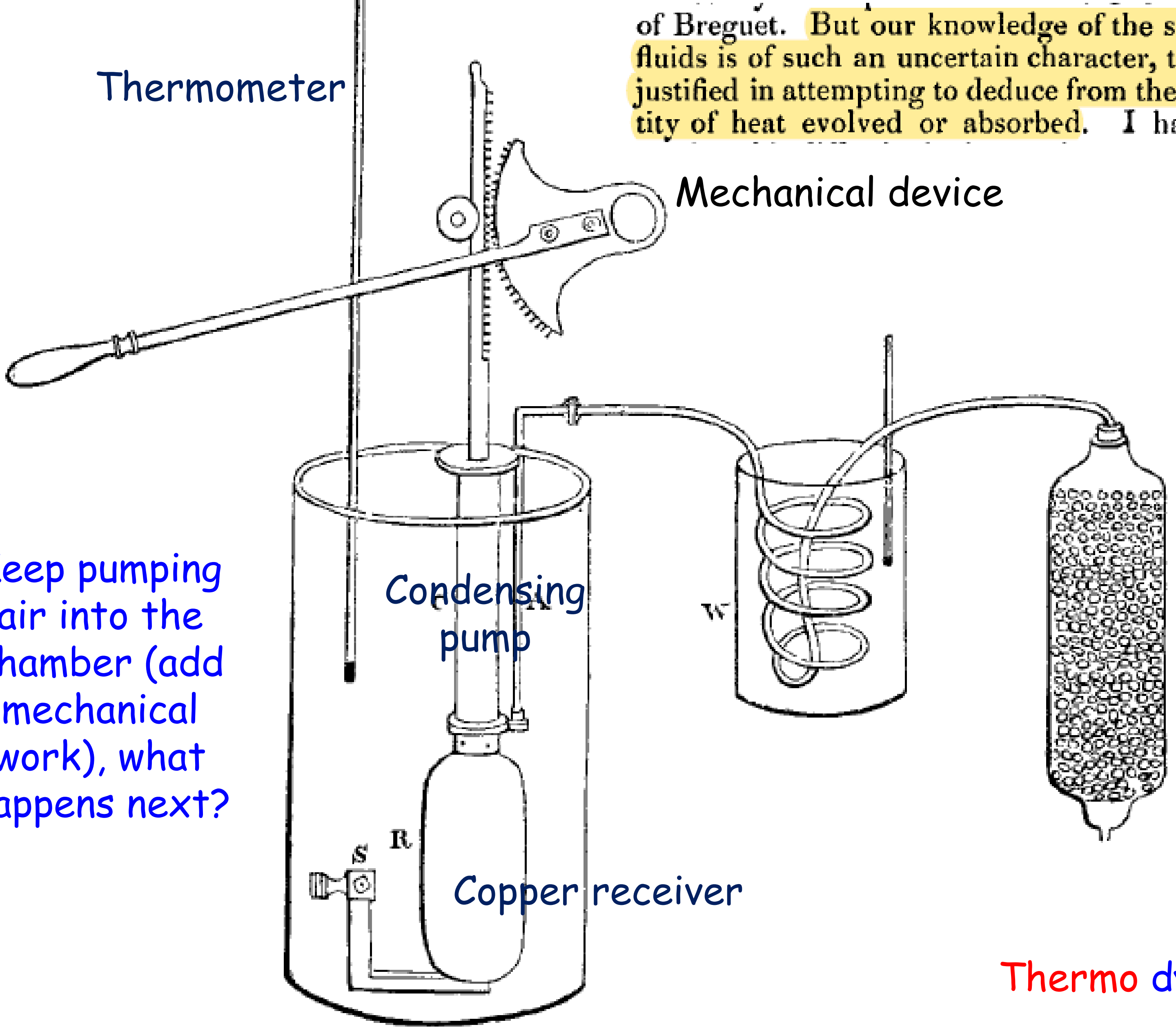
Structure of this lecture:

(1) Basics of thermodynamics
(2) Driving forces for phase transformations
(3) Thermodynamics of mixtures
(4) Understanding of phase diagrams
(5) Ternary phase diagrams
(6) High entropy alloys

Why is called thermodynamics?

James Prescott Joule (English, 1818-1889)
Image from Wikipedia

of Breguet. But our knowledge of the specific heat of elastic fluids is of such an uncertain character, that we should not be justified in attempting to deduce from them the absolute quantity of heat evolved or absorbed. I have succeeded in re-



Keep pumping air into the chamber (add mechanical work), what happens next?

The same amount of heat is always produced by the same amount of work

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* Memoirs of the Literary and Philosophical Society of Manchester, vol. v. part 2. p. 521–525.

Thermo dynamics

➢ Terminology and symbol

- Isolated system
- Closed system
- Isothermal process
- Adiabatic process
- Ideal solution
- non-ideal solution (real solution)
- Spontanoue (irreversible)

★ important equations

🏡 Self study

1. Basics

FIRST LAW of thermodynamics (and what follows):

Conservation of energy : energy can be transformed from one form to another, but can be neither created nor destroyed

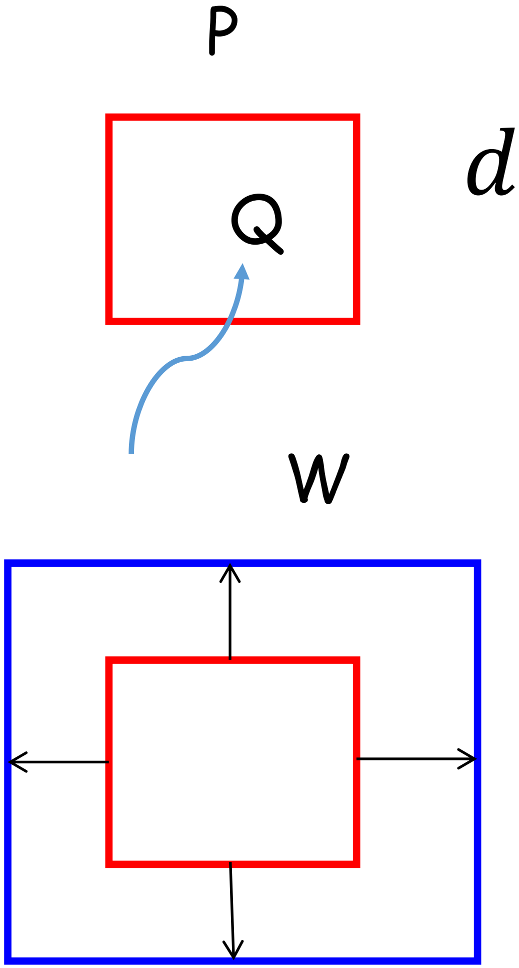
★

$$\boxed{dU = U_{II} - U_{I} = dQ + dW}$$

Thermodynamics is concerned with the beginning (U_I) and final states (U_{II}) of an isoalted system.

U – internal energy, Q – heat, W- work

$$dU = U_{II} - U_{I} = dQ + dW$$



$$dU = U_{II} - U_{I} = dQ - PdV$$

Heat capacity: heat adsorbed per unit change in temperature (dQ/dT)

At constant volume: $dU = \partial Q$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

We work at constant pressure, not at constant Volume. We define H:

$$dU = U_{II} - U_I = \partial Q - pdV = \partial Q - p(V_{II} - V_I)$$

We look at heat effect:

$$dQ = (U_{II} + pV_{II}) - (U_I + pV_I)$$

We introduce H: ★ $\boxed{H = U + pV}$

The enthalpy H of a thermodynamic system is defined as the sum of its internal energy and the product of its pressure and volume

Unit of Enthalpy: J/mol

U – internal energy, p-pressure, V-volume

We work with H:

$$H = U + pV \qquad H = f(T, p)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = dU + pdV + Vdp = \partial Q + Vdp$$

$$H = U + pV \qquad dU = \partial Q - pdV$$

Heat capacity at constant pressure

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p}$$

$$\boxed{\Delta H = \int_{T1}^{T2} C_p dT}$$

$$c_p = (\partial h / \partial T)_p = \frac{1}{n} \cdot C_p$$

Unit of heat capacity: J/k·mol

C_P – heat capacity, c_P – heat capacity per quantity of material,

n – number of moles

Materials engineers use empirical relations like

$$c_p = a + b \cdot T + c \cdot T^{-2} \ (in: \frac{J}{K \cdot mol})$$

with a, b und c from data bases.

Materials engineers often use the approximation of Dulong and Petit (which is a zero order approximation of idea gas:

$$c_p \approx 3R$$

R – universal gas constant

Related to FIRST LAW:

From which to which? Direction?

Conservation of energy : energy can be transformed from one form to another, but can be neither created nor destroyed

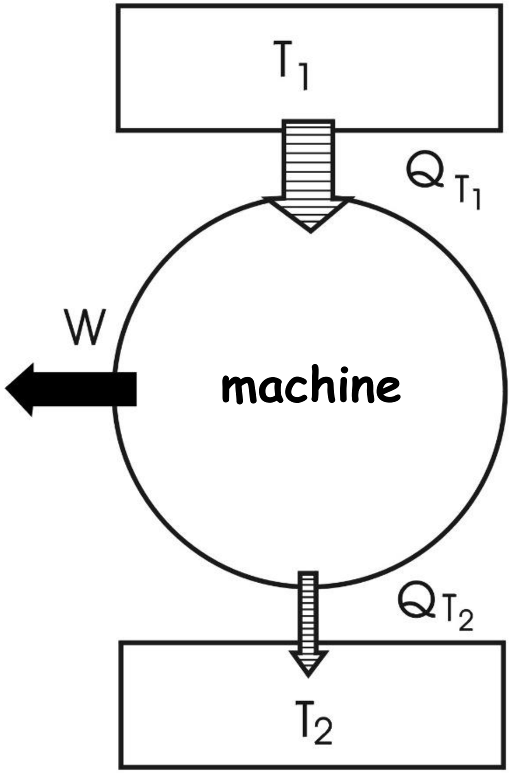
differential equations and characteristic functions

U – internal energy

H - enthalpy

c_p – heat capacity (how H depends on temperature)

SECOND LAW of thermodynamics:

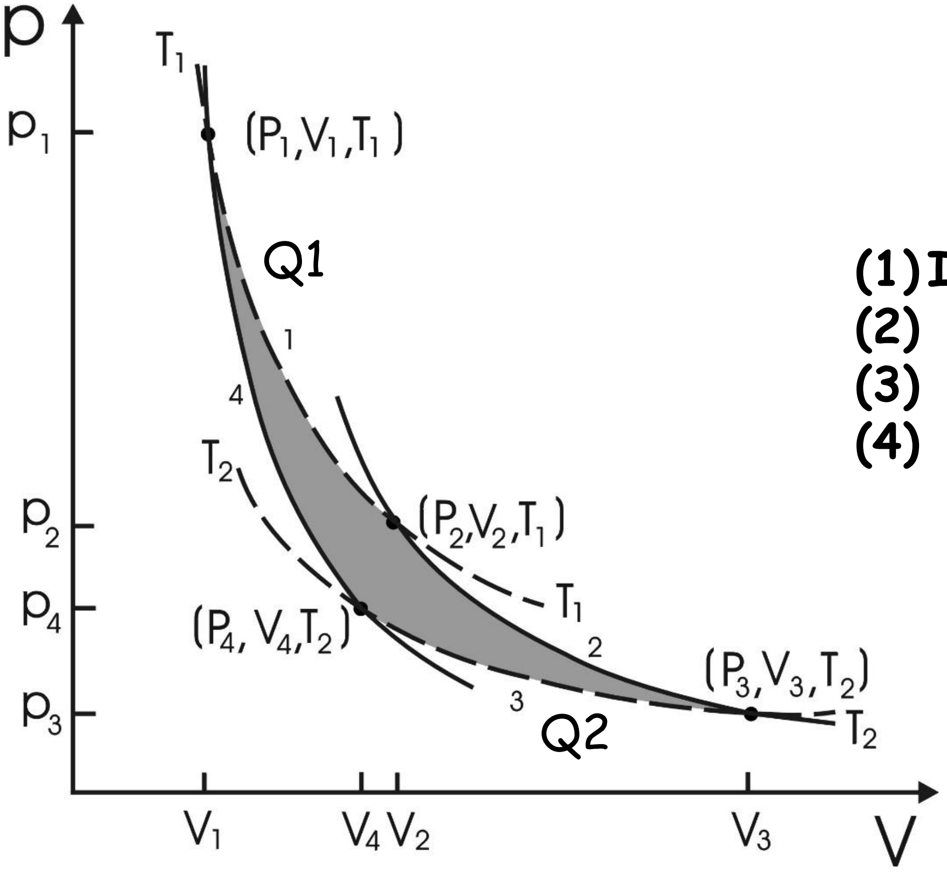


We cannot transform 100% heat (Q_{T1}) into work. We can transform some of it into work W. We must always produce waste heat Q_{T2}.

The efficiency η of our process is always smaller than 1:

$$\eta = 1 - T_2 / T_1$$

One can analyze an ideal process, known as the Carnot process. It involves an ideal gas which can transform heat/work into work/heat by expansion/compression. The Carnot process does what we have seen in the previous figure. It can be subdivided into four steps:



(1) Isothermal expansion (T1)
(2) Adiabatic expansion (T1-> T2)
(3) Isothermal compression (T2)
(4) Adiabatic compression (T2-> T1)

$$Q1/T1+Q2/T2=0$$

The Carnot process has been analyzed in detail. A number of important conclusions could be drawn, like:

(1) No processes have a higher efficiency than the Carnot process.

(2) The thermal efficiency of the Carnot process is smaller than 1.

This is of interest for questions related to energy conversion.

In materials science we are interested in spontaneous processes. Does something happen? Can we make an alloy? Does a melt solidify? Do carbides preciptitate? We want to have a parameter which gives us an answer to these questions. In this context it was interesting to find:

(3) When each step in the Carnot process is reversible, then the sum of the reduced heats is zero: $\sum Q/T=0$.

S (entropy)

(4) When one spontaneous (non reversible) process occurs, the sum of the reduced heats is >0.

We use the entropy S to describe a reduced heat:

★

$$dS = dQ / T$$

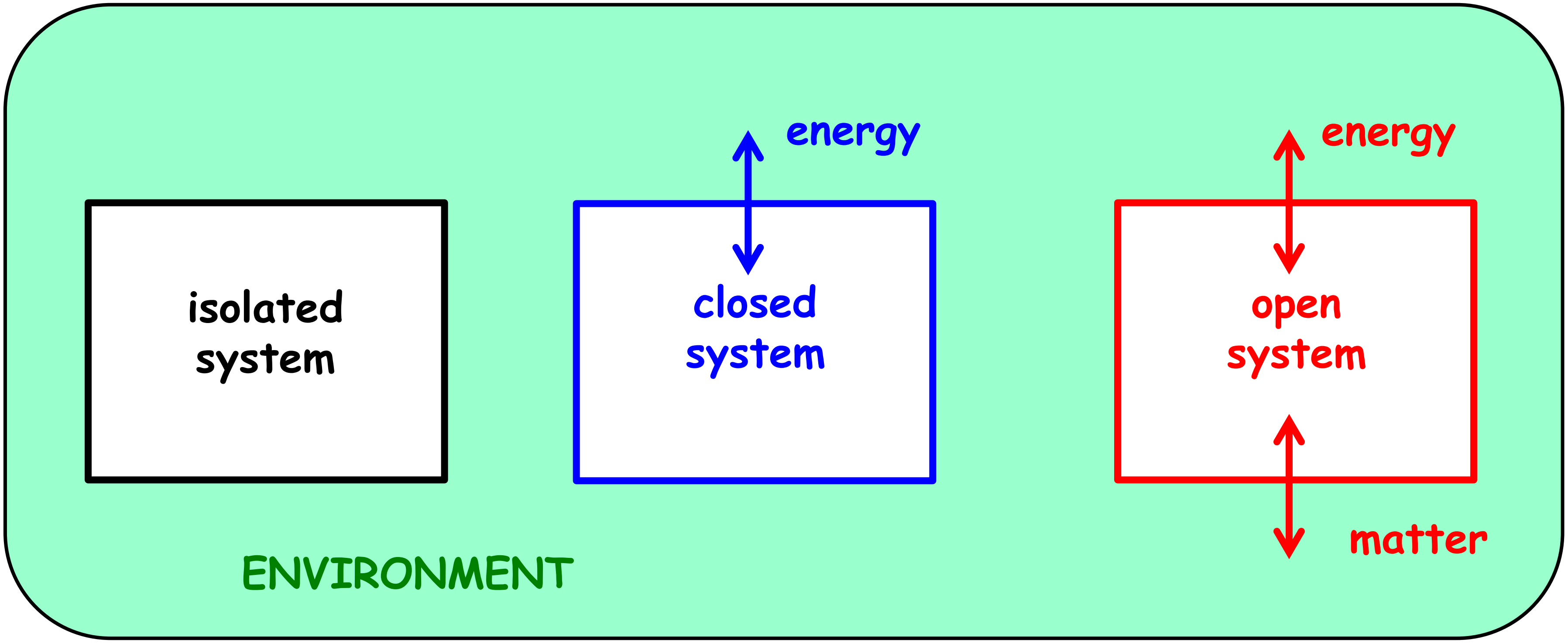
Unit of entropy: J/K·mol

Our analysis has shown, that when a system changes from state 1 into state 2, then we can differentiate to cases:

in equilibrium: $S_2 - S_1 = \Delta S = 0$

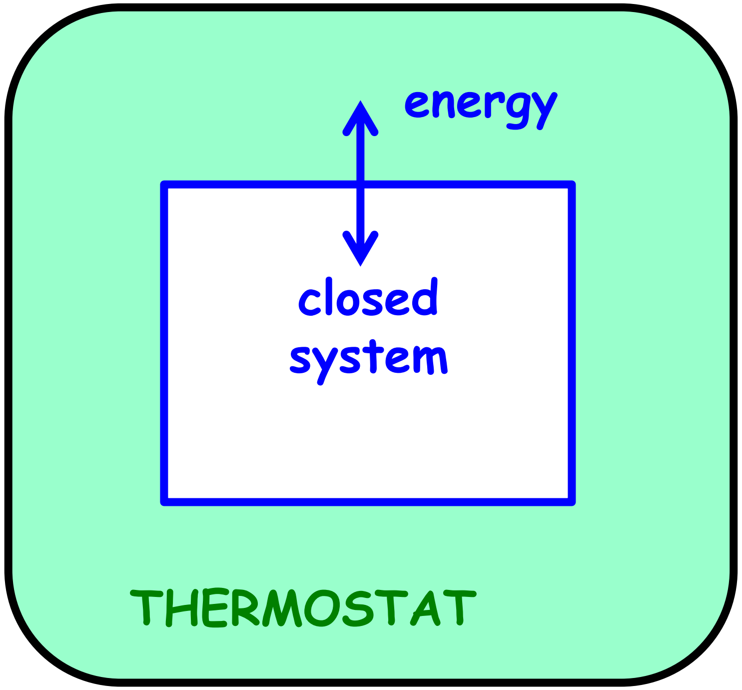
★

spontaneous process: $S_2 - S_1 = \Delta S > 0$



Carnot cycle occurs in an <u>isolated system</u>. ΔS=0: nothing happens. ΔS>0: spontaneous process.

However, in materials research we are interested in closed and open systems. E.g., alloy melt in crucible during melting, alloy melt in mould during solidification, steel specimen in furnace during heat treatment
→ closed systems.



In order to derive such an equation of state for our closed system, we consider our closed system together with its direct enviroment, and we assume, that the whole system represents an isolated system.

The direct enviroment is so big, that it behaves like a thermostat and does not notice a small heat transfer Q_{rev} into our closed system.

For spontaneous effect to occur in whole system:

$$dS_{isolated\ system} = dS_{closed\ system} + dS_{thermostat} \geq 0$$

$$dS_{\text{isolated system}} = dS_{\text{closed system}} + dS_{\text{thermostat}} \geq 0$$

$$dQ_{\text{closed system}} = -dQ_{\text{thermostat}}$$

we can write:

$$dS_{\text{isolated system}} = dS_{\text{closed system}} - \frac{\delta Q_{\text{closed system}}}{T} \geq 0$$

$$dS_{\text{closed system}} - \frac{\delta H_{\text{closed system}}}{T} \geq 0$$

$$TdS_{\text{closed system}} - dH_{\text{closed system}} \geq 0$$

★

$$\boxed{dH_{\text{closed system}} - TdS_{\text{closed system}} \leq 0}$$

We introduce the **Gibbs free energy G**:

$$dG = dH_{\text{closed system}} - TdS_{\text{closed system}} \leq 0$$

with this we get:

★

$$\boxed{G = H - T \cdot S}$$

Unit of G: J/mol

G is the state function which we need in our closed systems. It provides information about a process. $\Delta G=0$: equilibrium - nothing happens. $\Delta G<0$: we have a driving force for a spontaneous process.

ΔG as driving force for spontaneous processes in closed systems:

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

For a high driving force ΔG we want an as negative as possible ΔH (heat comes out of system) and a high positive ΔS. We see that the influence of the ΔS-term ($T \cdot \Delta S$) increases with increasing temperature.

What is the physical meaning?

Ludwig Boltzmann

20.2.1844-5.Sept.1906

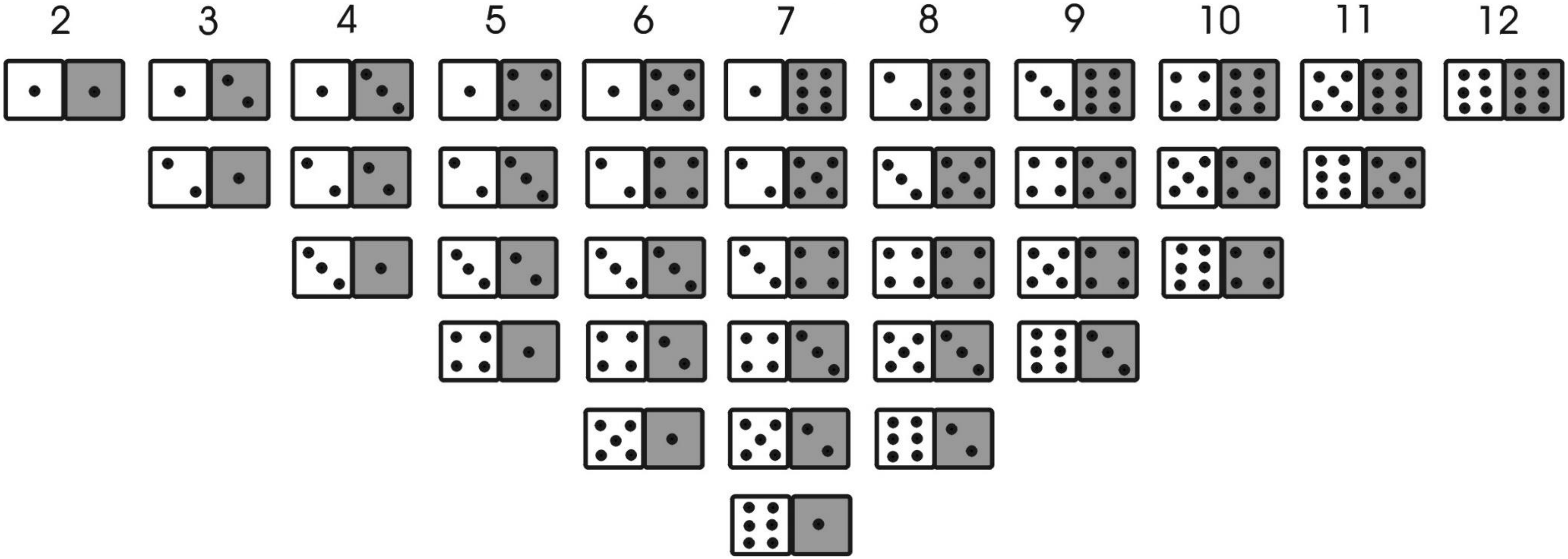
grave:

Wiener Zentralfriedhof

Foto: 14. May 2016

(from Internet)

Playing dice (example)



The macro state 7 is more probable than the macro state 2, because it has a higher number of possible micro states! Imagine we had 6,023·10^{23} dice (1 mol of ideal gases)

Famous and important statistical interpretation of entropy S by Ludwig Boltzmann:

★

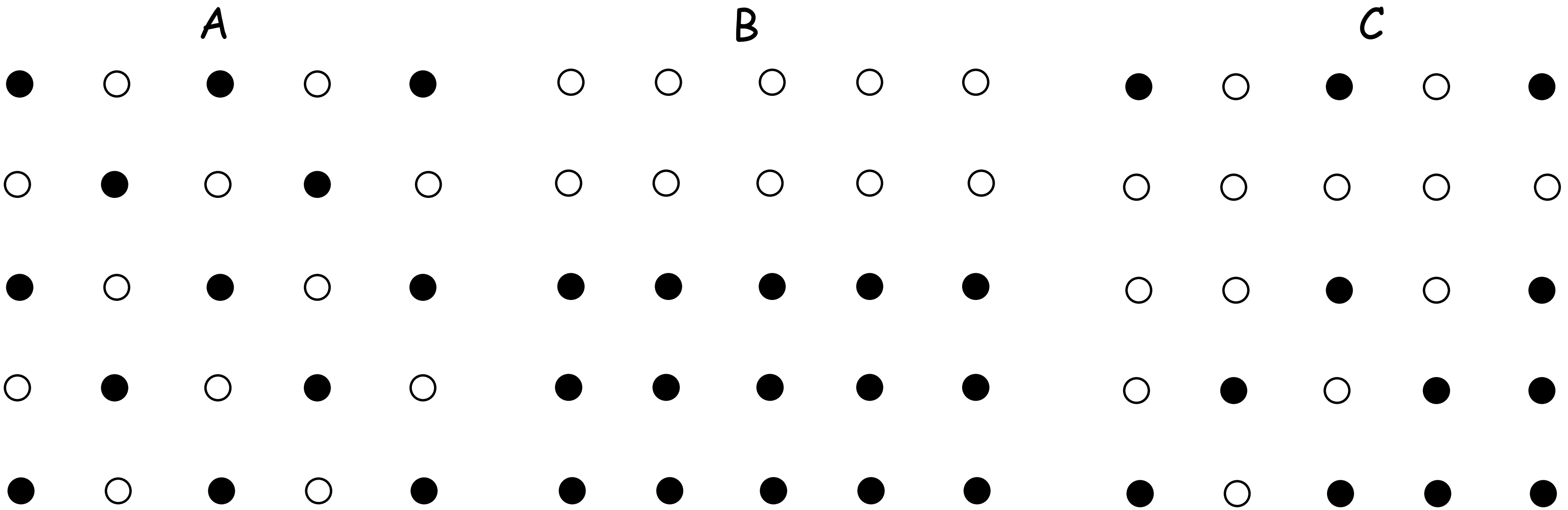
$$\boxed{S = k_B \cdot \ln \omega}$$

There is a macrostate which has the entropy S.

ω is the number of micro states which correponds to this macro state.

k_B is the Boltzmann constant 1,381 $\cdot 10^{-23}$ JK^{-1}. k_B is for an atom, what R is for one mole: R = $N_A \cdot k_B$ (NA – Avogadro Zahl von Teilchen in einem Mol: 6,023 $\cdot 10^{23}$ mol^{-1}.

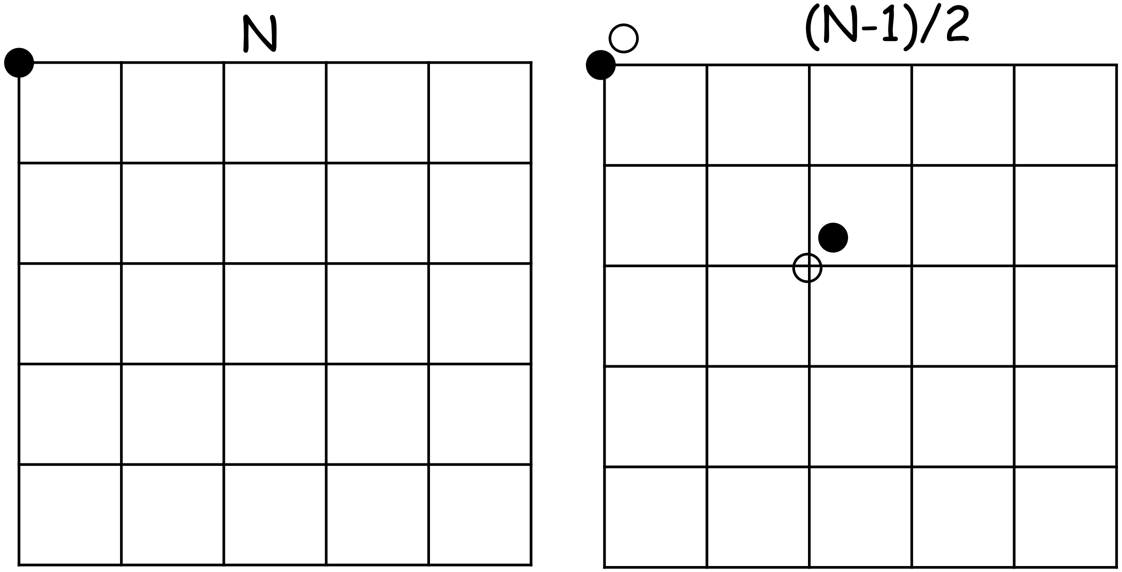
For solid solution



Which has a higher probability?

Nature establishes the macro state which corresponds to the highest number of microstates = which has the highest probability.

For solid solution



$$\frac{N(N-1)\ldots(N-n+2)(N-n+1)}{n!}$$

$$w=\frac{N!}{n!\,(N-n)!}$$

Boltzmann's equation:

$$\Delta S^M = k_B \cdot \ln \omega = k_B \cdot \ln\left(\frac{N!}{N_1! \cdot N_2!}\right)$$

From this with Stirling's approximation for large numbers (ln N! = N·ln N – N) and by introducing mole fractions we obtain:

★

$$\boxed{\Delta S^M = -R \cdot (x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2)}$$

x1 and x2: mole fractions of 1 and 2 atoms, R is gas constant

Related to SECOND LAW:

Carnot process

Entropy S

ΔS as driving force in isolated system

Gibbs free energy G

ΔG as driving force in closed system

Statistical interpretation of entropy S: aims at establishing the highest degree of disorder. This tendency increases with increasing temperature.

2. THERMODYNAMICS OF PHASE TRANSFORMATIONS

Example: The martensitic transformation

$$\mathit{austenite} \leftrightarrow \mathit{martensite}$$

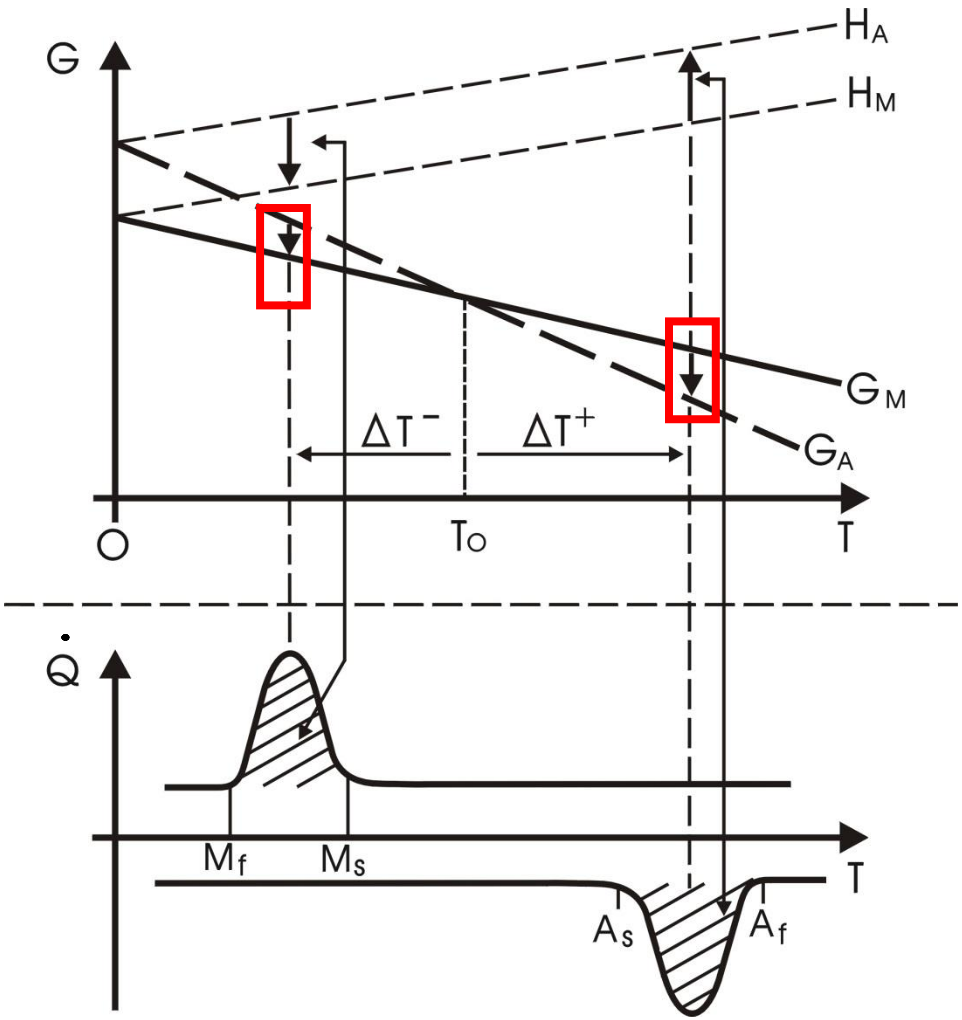
On cooling from high T (forward transformation):

$$\mathit{austenite} \rightarrow \mathit{martensite}$$

On heating from low T (reverse transformation):

$$\mathit{martensite} \rightarrow \mathit{austenite}$$

We have made a big step when we understand this schematic diagram:

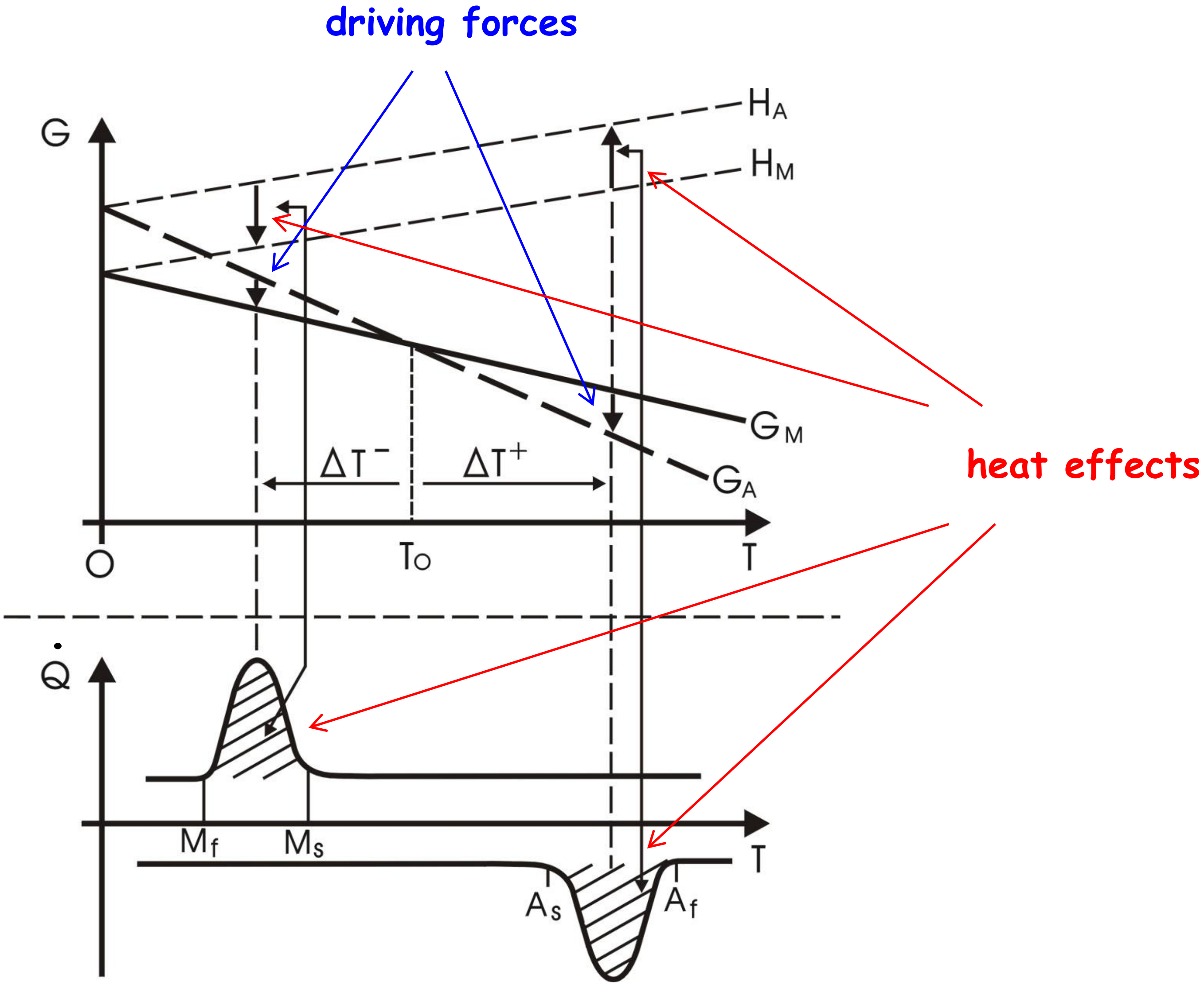


G(T)-curves

H(T)-curves

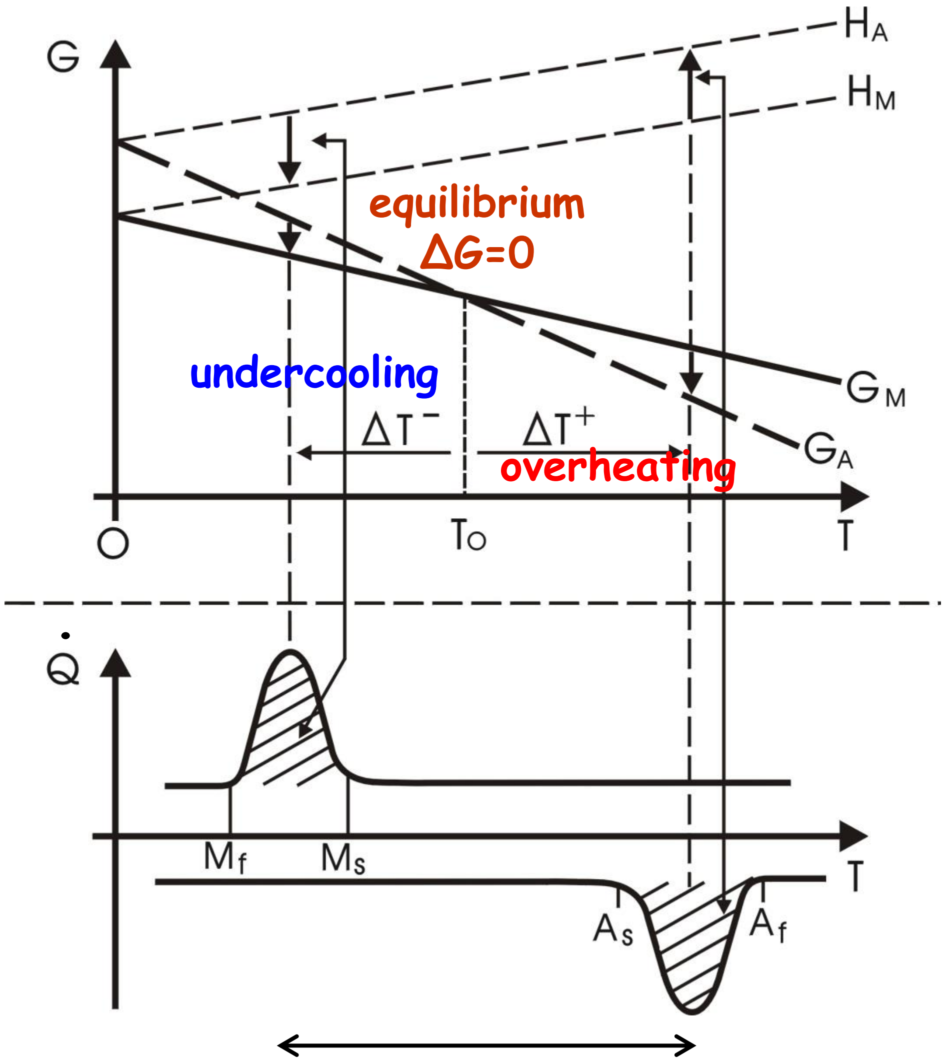
ΔG – DRIVING FORCE – ALWAYS NEGATIVE – LITTLE ARROWS POINTING DOWN

DSC chart



driving forces

heat effects



equilibrium
$\Delta G=0$

undercooling

overheating

hysteresis

thermodynamic
background

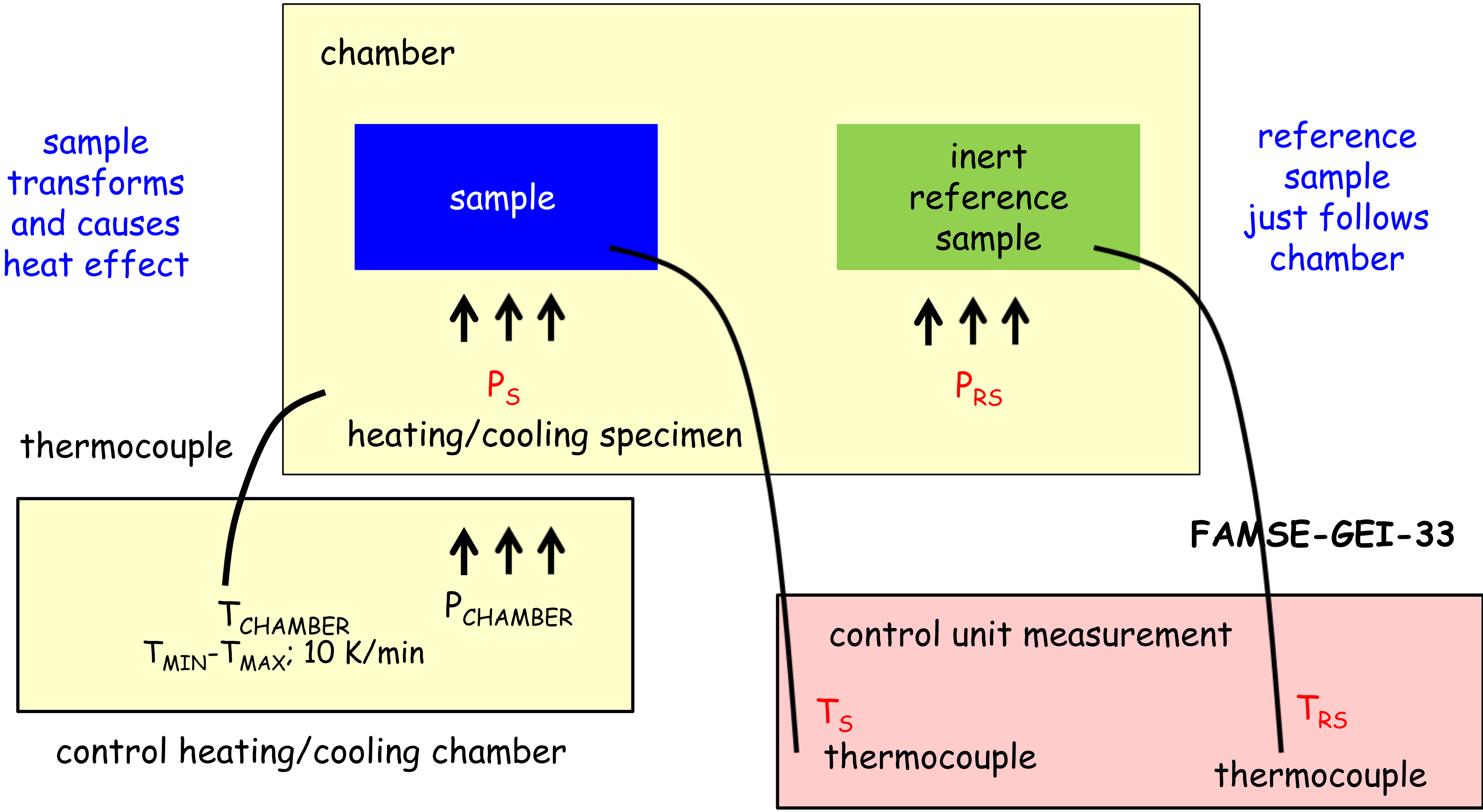
experiment

Differential Scanning Calorimetry

DSC

Control circuit keeps both specimens at same temperature: $T_S = T_{RS}$

Measurement: $\Delta P = P_S - P_{RS}$ (direct measurment of electric energy)



sample transforms and causes heat effect

chamber

sample

P_S

heating/cooling specimen

inert reference sample

P_{RS}

reference sample just follows chamber

thermocouple

$T_{CHAMBER}$

T_{MIN}-T_{MAX}: 10 K/min

$P_{CHAMBER}$

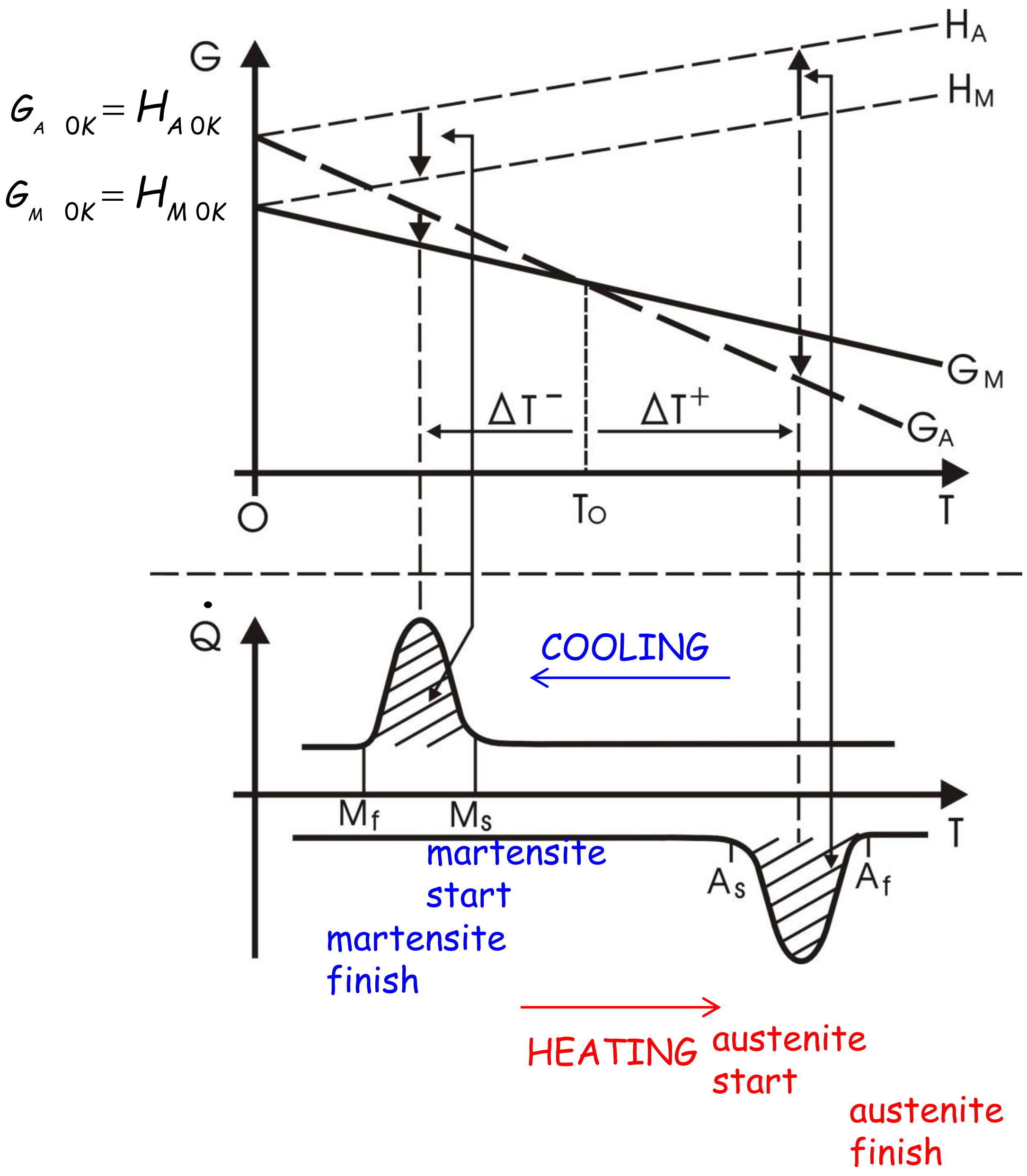
control heating/cooling chamber

control unit measurement

T_S thermocouple

T_{RS} thermocouple

EQUATIONS/APPROXIMATIONS



$$c_p = const. = 3R$$

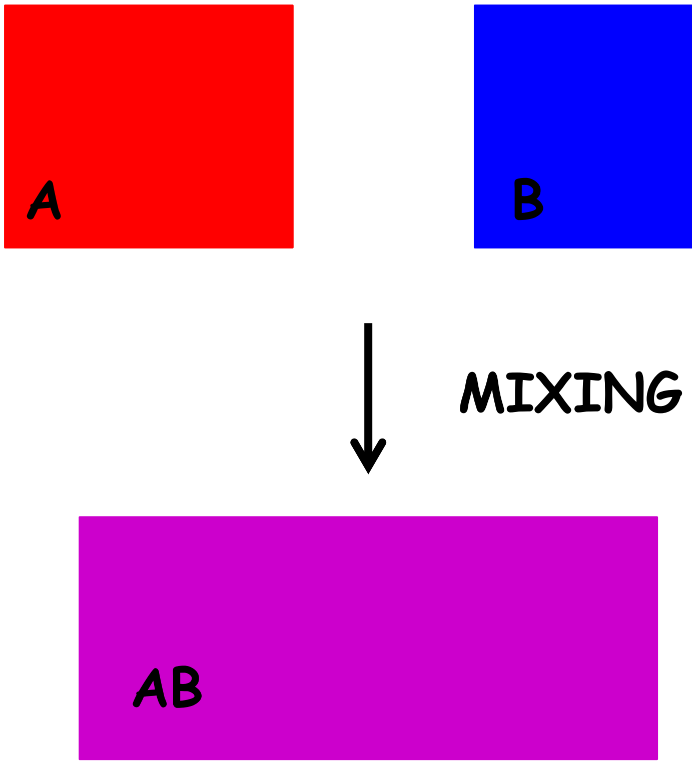
$$H = H_0 + \int_0^T c_p \, dT$$

DSC EXPERIMENT

cooling / heating rate: 10 K/min

3. THERMODYNAMICS OF MIXTURES

This is the basis for the understanding of alloys and of phase diagrams!



pure elements

homogeneous solution

We remember:

There are daily life systems which mix:

sugar/tea, wine/water, …

There are other systems we know which do not mix:

oil/water, ….

There is mixing without any special effects:

We just add everything up and get the correct result.

$$V_{AB} = n_A \cdot V_A + n_B \cdot V_B \qquad G_{AB} = n_A \cdot G_A + n_B \cdot G_B$$

(here: V – molar volume, n – number of moles)

This is simple. We call such solutions ideal solutions. These are actually not so very interesting.

It is more interesting when there is an effect of mixing, like for example:

$$V_{AB} < n_A \cdot V_A + n_B \cdot V_B \qquad G_{AB} > n_A \cdot G_A + n_B \cdot G_B$$

How do we deal with effects of mixing?

A simple physical system which allows to directly address the interaction of atoms in a binary systems

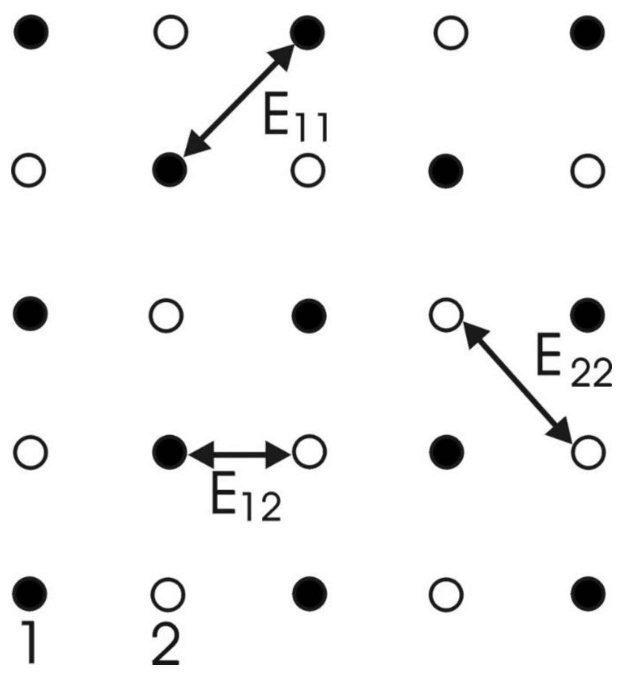
$$G_{AB} = n_A G_A + n_B G_B + \Delta G^M \qquad \Delta G^M = \Delta H^M - T\Delta S^M$$

We calculate for mixtures:

Excess terms: ΔG^M, ΔH^M and ΔS^M of mixture

ΔH^M contribution

Our system and our approximations:

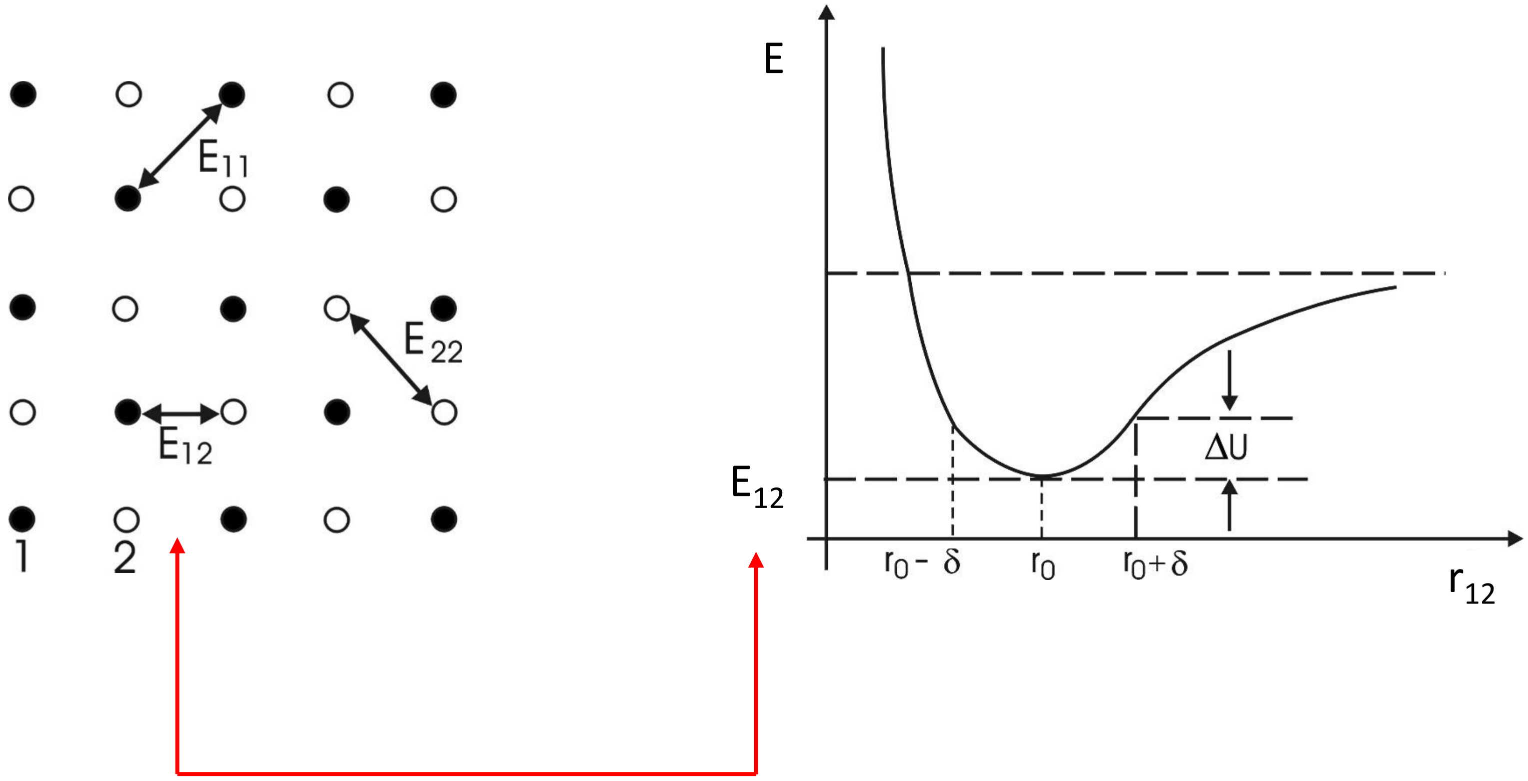


System (crystal) with two Types of atoms (1-black, 2-white).

We only consider next neighbour interactions.

There are three of these: E_{11}, E_{22}, E_{12}

When we see a E_{12}-term, we remember that there is a bonding energy between atoms 1 and 2!



We add everything up and obtain:

Enthalpy of mixture (which we can measure):

★

$$\boxed{\Delta H^{M} = z \cdot x_1 \cdot x_2 \cdot W}$$

z: number of neighbours, x1 and x2: mole fractions of 1 and 2 atoms,
W: interaction term

Interaction term W (which we understand):

★

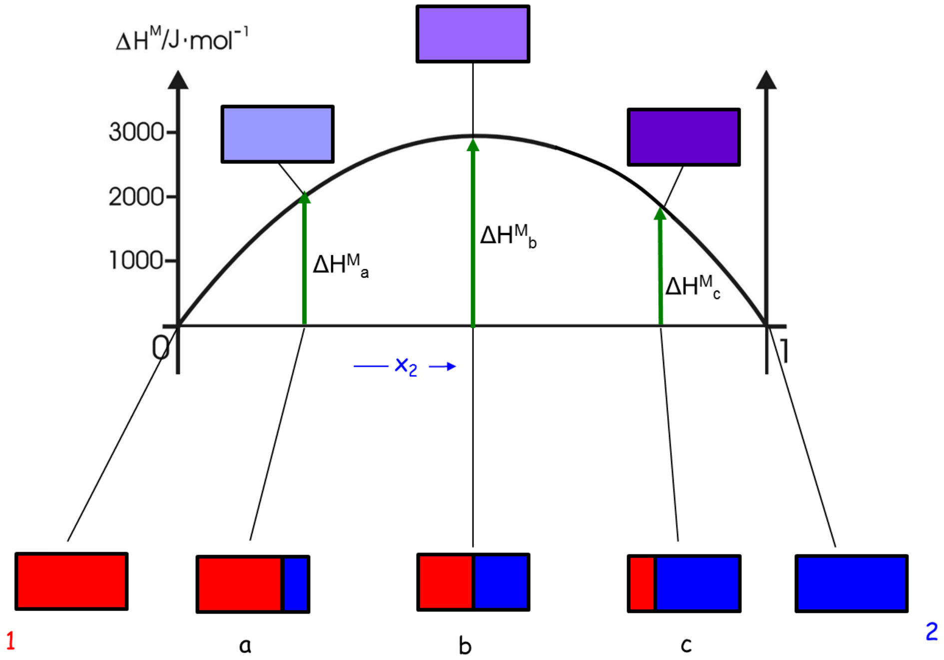
$$\boxed{W = E_{12} - \frac{1}{2} \cdot (E_{11} + E_{22}) = E_{12} - \bar{E}}$$

$E_{11} + E_{22} < 2E_{12}$: favors ordering, $W > 0$

$E_{11} + E_{22} > 2E_{12}$: favors clustering, $W < 0$

E_{ii}: binding energies between atoms i and i

We plot ΔH^M as a function of x_2. We see the whole system. Here we consider a case, where there is a repulsive type of interaction ($\Delta H^M > 0$). We need to provide energy for mixing!



(1)We consider the mixing of two components, 1 (red) and 2 (blue).

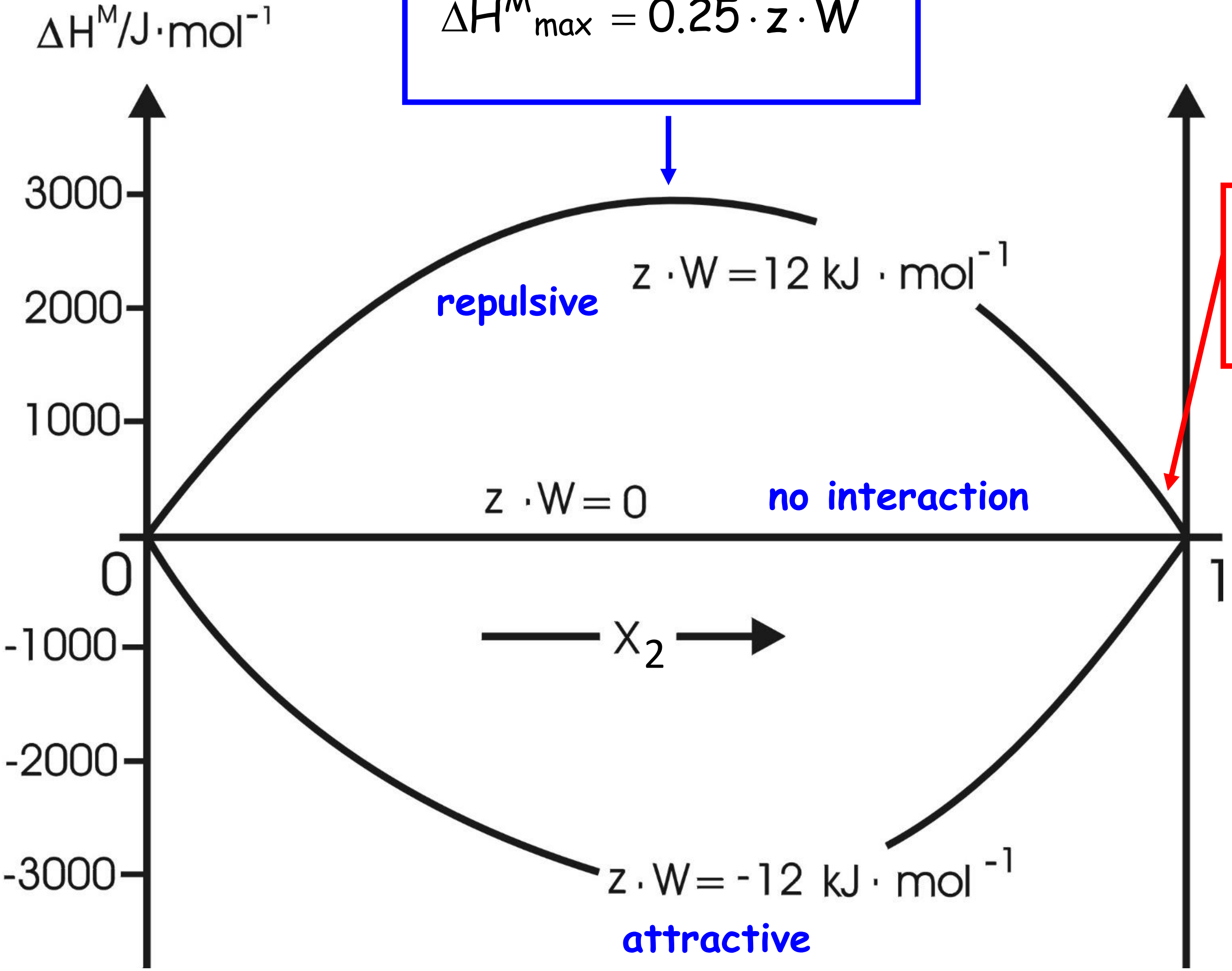
(2) On the x-axis we plot all alloy compositions, which gradually change from pure 1 (red, $x_2=0$) to pure 2 (blue, $x_2=1$)

(3) On the y-axis we plot the heat of transformations.

(4) We show the heats of transformation for three alloy compositions (green arrows).

(5) Our $\Delta H^M(x)$-curve runs through 0 at $x_2 = 0$ and 1. Pure elements do not mix!

$$\Delta H^M{}_{max} = 0.25 \cdot z \cdot W$$



$$\lim_{x_1 \to 1} \frac{\partial \Delta H^M}{\partial x_1} = -z \cdot W$$

Finite slope!

$$\Delta H^M = z \cdot x_1 \cdot x_2 \cdot W \qquad W = E_{12} - \frac{1}{2} \cdot (E_{11} + E_{22}) = E_{12} - \bar{E}$$

So far we know what the bond energy between the atoms of our two component system does. It is responsible for the enthalpy of mixture:

$$\boxed{\Delta H^M = z \cdot x_1 \cdot x_2 \cdot W \quad \text{with} \quad W = E_{12} - \frac{1}{2} \cdot (E_{11} + E_{22}) = E_{12} - \bar{E}}$$

For a complete picture we need to know the Gibbs free energy of mixture:

$$\boxed{\Delta G^M = \Delta H^M - T \cdot \Delta S^M}$$

What about the entropy term $\boxed{-T \cdot \Delta S^M}$?

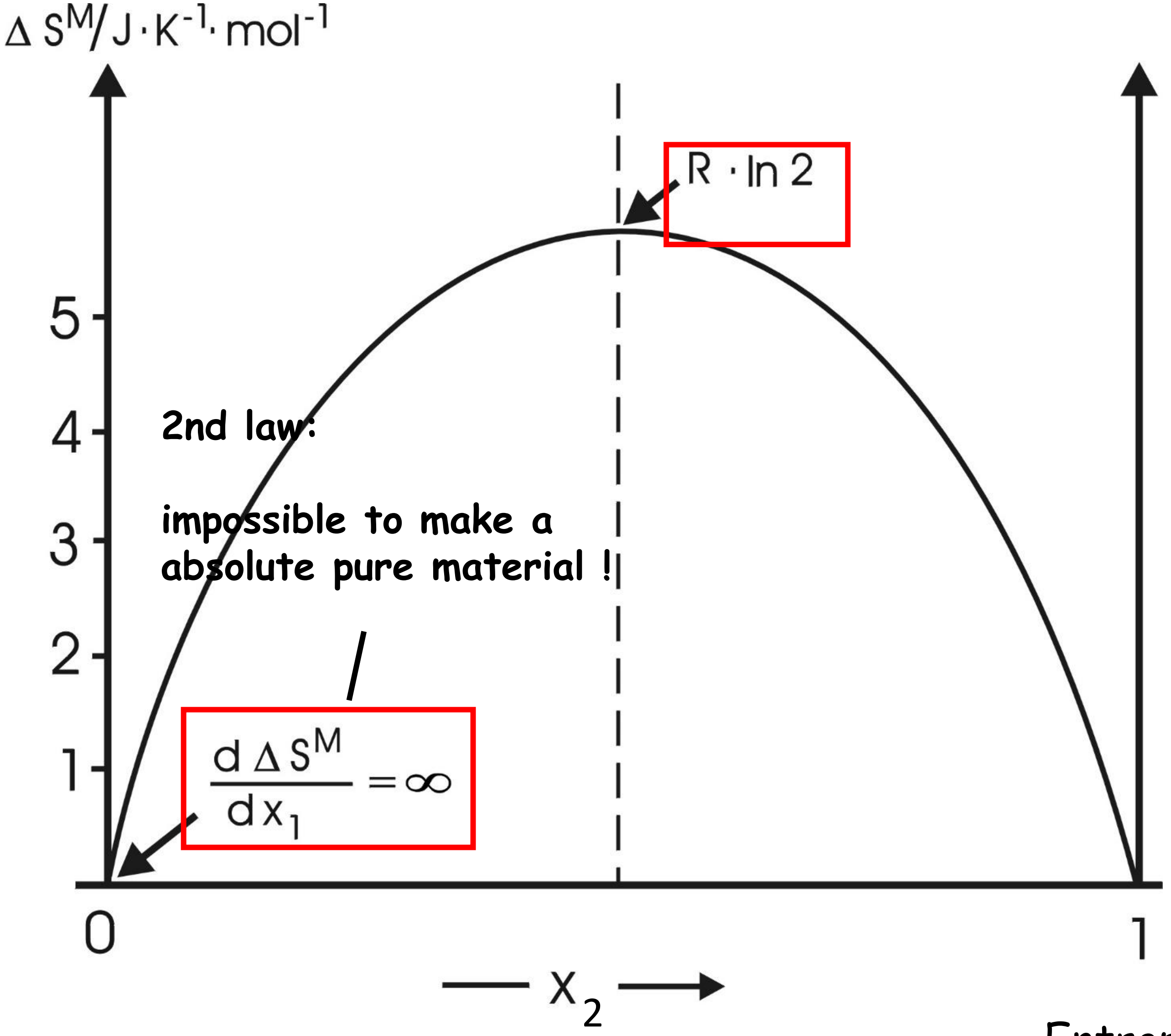
Boltzmann's equation:

$$\Delta S^M = k_B \cdot \ln \omega = k_B \cdot \ln\left(\frac{N!}{N_1! \cdot N_2!}\right)$$

From this with Stirling's approximation for large numbers (ln N! = N·ln N – N) and by introducing mole fractions we obtain:

$$\boxed{\Delta S^M = -R \cdot (x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2)}$$

x1 and x2: mole fractions of 1 and 2 atoms, R is gas constant



2nd law:

impossible to make a absolute pure material !

Entropy of mixing

$$\Delta S^M = -R \cdot (x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2)$$

If we first consider an ideal solid solution:

$$\Delta G^M = \Delta H^M - T \cdot \Delta S^M$$

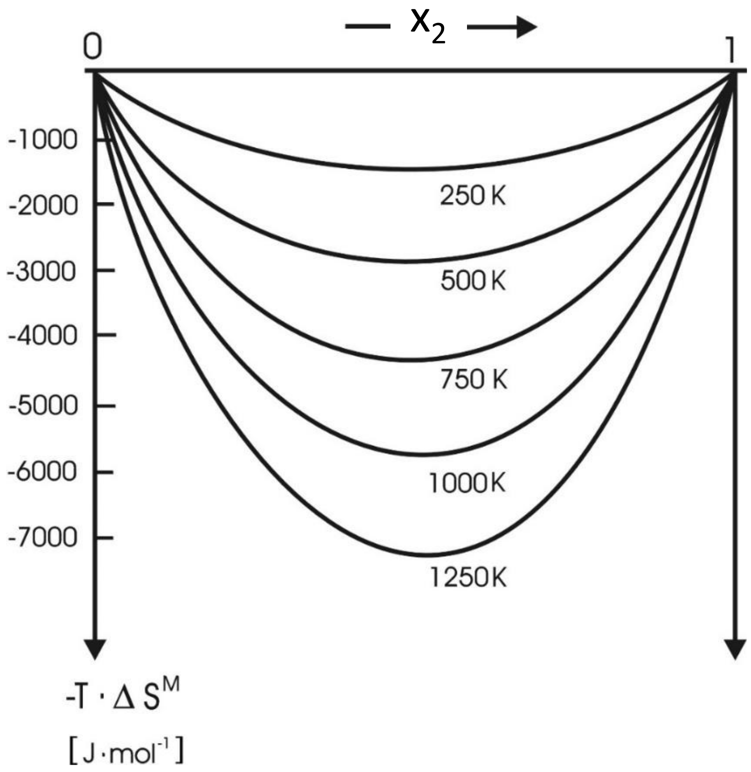
ideal: W=0, ΔH=0

$$\Delta G^M = -T \cdot \Delta S^M = R \cdot T \cdot (x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2)$$

Ideal solution: ΔG^M is given by the entropy term!

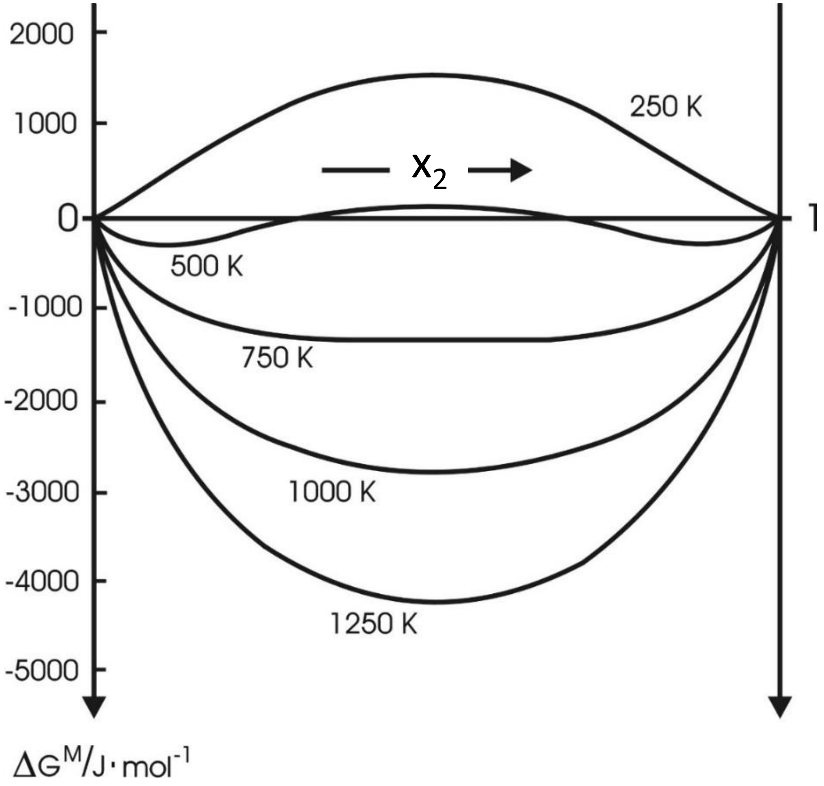
The Gibbs free energy of mixing of an ideal system (ΔH^M=0)

$$\Delta G^M = -T \cdot \Delta S^M = R \cdot T \cdot (x_1 \cdot \ln x_1 + x_2 \cdot \ln x_2)$$



Ideal solution (ΔH^M=0):

Now we consider the interesting case: a real solid solution with repulsive interaction ($\Delta H^M>0$):

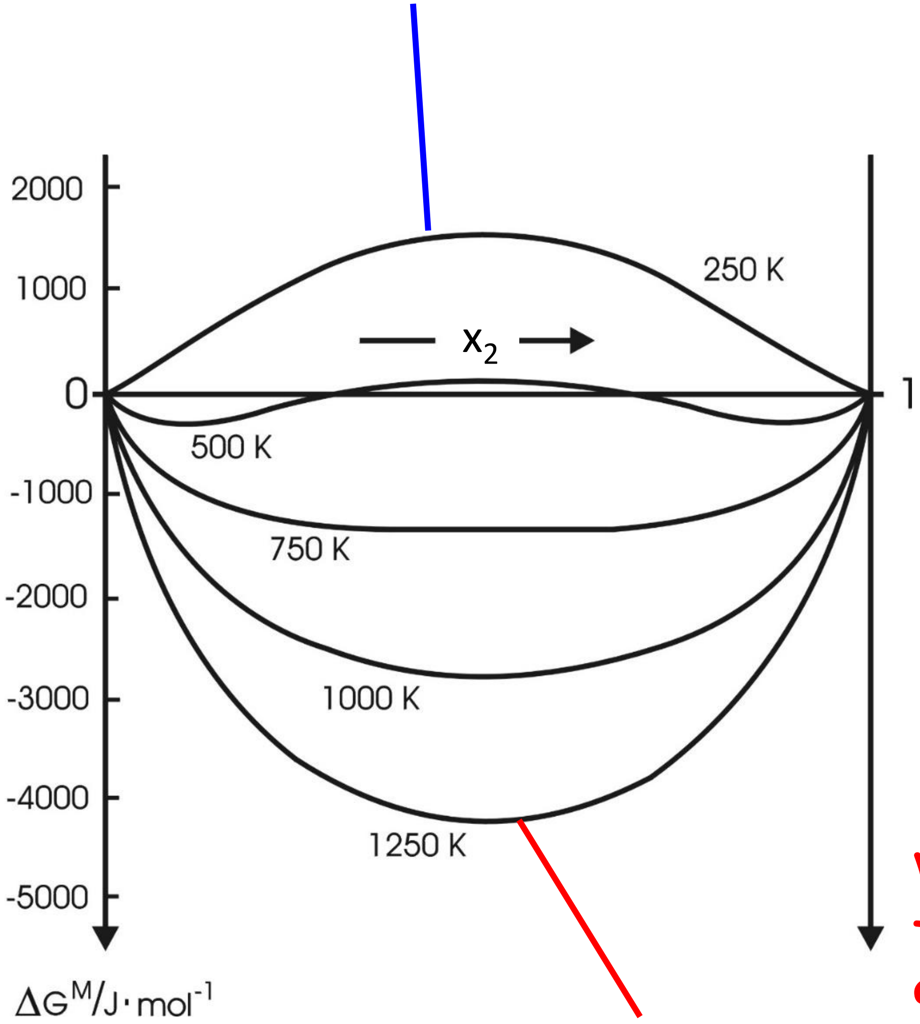


$$\Delta G^M = \Delta H^M - T \cdot \Delta S^M =$$

$$= z \cdot x_1 \cdot x_2 \cdot W +$$
$$+ RT \cdot (x_1 \ln x_1 + x_2 \ln x2)$$

The Gibbs free energy of a real system with repulsive interaction ($\Delta H^M>0$).

low T: positive ΔH^M-term (repulsive interaction) dominates! no mixing!



$$\Delta G^M = \Delta H^M - T \cdot \Delta S^M =$$

$$= z \cdot x_1 \cdot x_2 \cdot W +$$
$$+ RT \cdot (x_1 \ln x_1 + x_2 \ln x2)$$

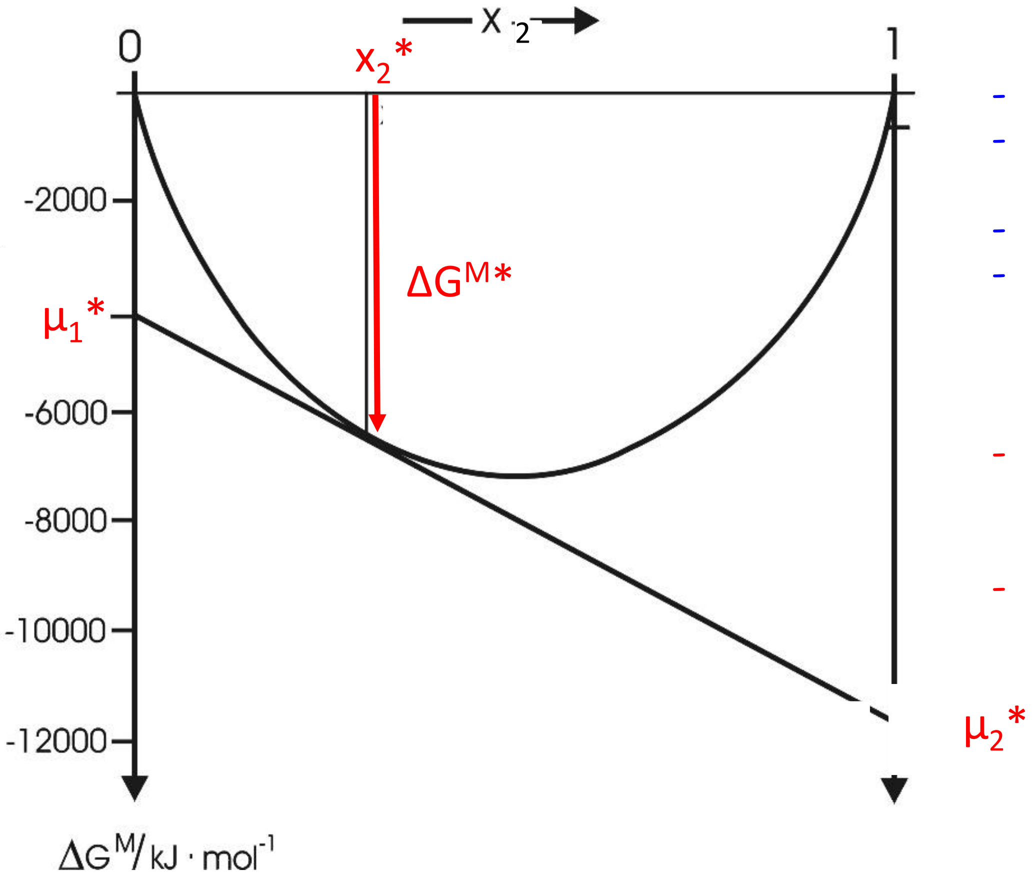
With increasing temperature, the entropy term becomes more and more important!

high T: $-T \cdot \Delta S^M$-term dominates! mixing!

Another way to look at G(x)-plot (for an ideal solution)

$\Delta H^M = 0$

Figure PT.20: Tangent construction.



- we select an alloy composition x_2^*
- we know ΔG^{M*}, the driving force for mixing
- at x_2^* we draw a tangent to the G(x)-curve
- where the tangent intersect the axes we have the chemical potentials of the components 1 and 2

- μ_1^*: chemical potential of component 1 in alloy of composition x_2^*

- μ_2^*: chemical potential of component 1 in alloy of composition x_2^*

$$\frac{dG}{dx_2} = \mu_2 - \mu_1$$

$$\Delta G^{M*} = (1 - x_2^*)\, \mu_1^* + x_2^*\, \mu_2^*$$

What is the physical meaning of μ ?

If a small amount of A, dn_A mol, is added to a large amount of a phase at constant temperature and pressure, the free energy change $d\bar{G}$ is equal to:

$d\bar{G} = \mu_A \, dn_A$

★

$$\boxed{\mu_A = \left(\frac{\partial \bar{G}}{\partial n_A}\right)_{T,p,n_B}}$$

chemical potential of the component *A*

↑

we keep everything else constant

μ_A is called chemical potential or partial molar free energy of A in the phase.

μ_A depends on the composition of the phase.

What is the chemical potential μ ?

$$\mu_{Zn\ in\ brass\ with\ 10\%Zn} = \left(\frac{\partial G_{brass}}{\partial n_{Zn}} \right)_{T\ ,p\ ,n_{Cu}}$$

μ_{Zn} tells us how much the *G* of brass changes, when we add one mole of Zn.

Meaningless to say: the μ of Zn.

We must say: the μ of Zn in a brass with 10%Zn.

What about dG?

Gibbs: The change in G of a homogeneous part of the system must Be related to the changes of the masses of the substances:

$$dG = -SdT + Vdp + \boxed{\sum_{1}^{n} \mu_i \cdot dx_i}$$

for T, p = const. and binary system: $dG = \mu_1 \, dx_1 + \mu_2 \, dx_2$

with: $dx_1 = -dx_2$

$$dG = (\mu_2 - \mu_1) \, dx_2$$

$$\boxed{dG/dx_2 = \mu_2 - \mu_1}$$

Translation rule between G(x)- and μ-thermodynamics.

Concentration dependence of chemical potential:

For ideal gas:

$$dG = -SdT + Vdp$$

T=const.: $$dG = Vdp$$

pV=RT: $$dG = RT \cdot \frac{dp}{p}$$

integration: $$G = G_{p1} + RT \cdot \ln \frac{p_2}{p_1}$$

Concentrations:

mixture of gases: total pressure and partial pressures

$$p = \sum_{i}^{k} p_i$$

$$\frac{p_i}{p} = \frac{n_i RT/V}{\sum n_i RT/V} = \frac{n_i}{\sum n_i} = x_i$$

concentration

1000g Fe-C-alloy with 3 wt.-% C:

$$n_C = \frac{0.03}{12g/\text{mol}} \cdot 1000g = 2{,}5\ \text{mol}$$

moles C

$$n_{Fe} = \frac{0.97}{56g/\text{mol}} \cdot 1000g = 17{,}3\ \text{mol}$$

moles Fe

$$M_{Fe-3\%C} = \frac{1000g}{2{,}5\ \text{mol} + 17{,}3\ \text{mol}} = \frac{50{,}5g}{\text{mol}}$$

molecular weight of alloy

mole fractions of C and Fe

$$x_C = \frac{2{,}5\ \text{mol}}{2{,}5\ \text{mol} + 17{,}3\ \text{mol}} = 0{,}126$$

mole fraction of C

$$x_{Fe} = \frac{17{,}3\ \text{mol}}{2{,}5\ \text{mol} + 17{,}3\ \text{mol}} = 0{,}874$$

mole fraction of Fe

same for μ:

$$\mu = \mu_{p1} + RT \cdot \ln \frac{p_2}{p_1}$$

define reference condition: $\mu_i(p,T) = \mu_i{}^*(p_i,T)$

with this:

$$\mu_i(p,T) = \mu_i{}^*(p,T) + RT \cdot \ln \frac{p_i}{p} = \mu_i{}^*(p,T) + RT \cdot \ln x_i$$

★

$$\boxed{\mu_i(x) = \mu_i{}^{ideal} = \mu_i{}^0 + RT \cdot \ln x_i}$$

For ideal solution

Ideal solution:

★

$$\boxed{\mu_i(x) = \mu_i^{\mathrm{ideal}} = \mu_i^{0} + RT\cdot\ln x_i}$$

Regular non-ideal solution (activity: a = f·x):

$$\boxed{\mu_i = \mu_0 + RT\cdot\ln\left(f_i\cdot x_i\right)} = \mu_0 + RT\cdot\ln x_i + \boxed{RT\cdot\ln f_i}$$

↑

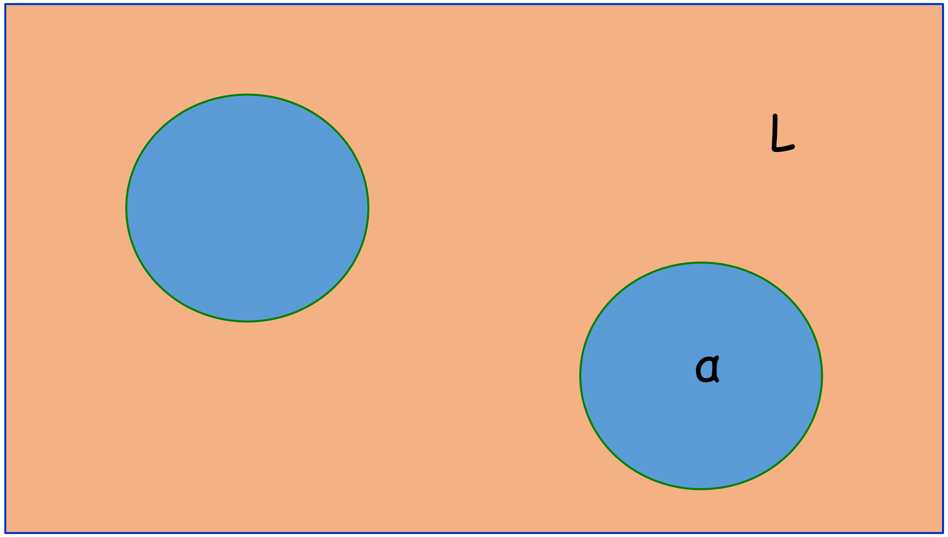
binary system:

$$f_1 = \exp\left(\frac{x_2^{2}\cdot z\cdot W}{RT}\right) \qquad f_2 = \exp\left(\frac{x_1^{2}\cdot z\cdot W}{RT}\right)$$

→ **atomic interactions**

→ The tendency of an atom to leave a solution

Equilibrium between two phases (example: system AB with a liquid phase L and a solid phase α):



L: 70% A, 30% B

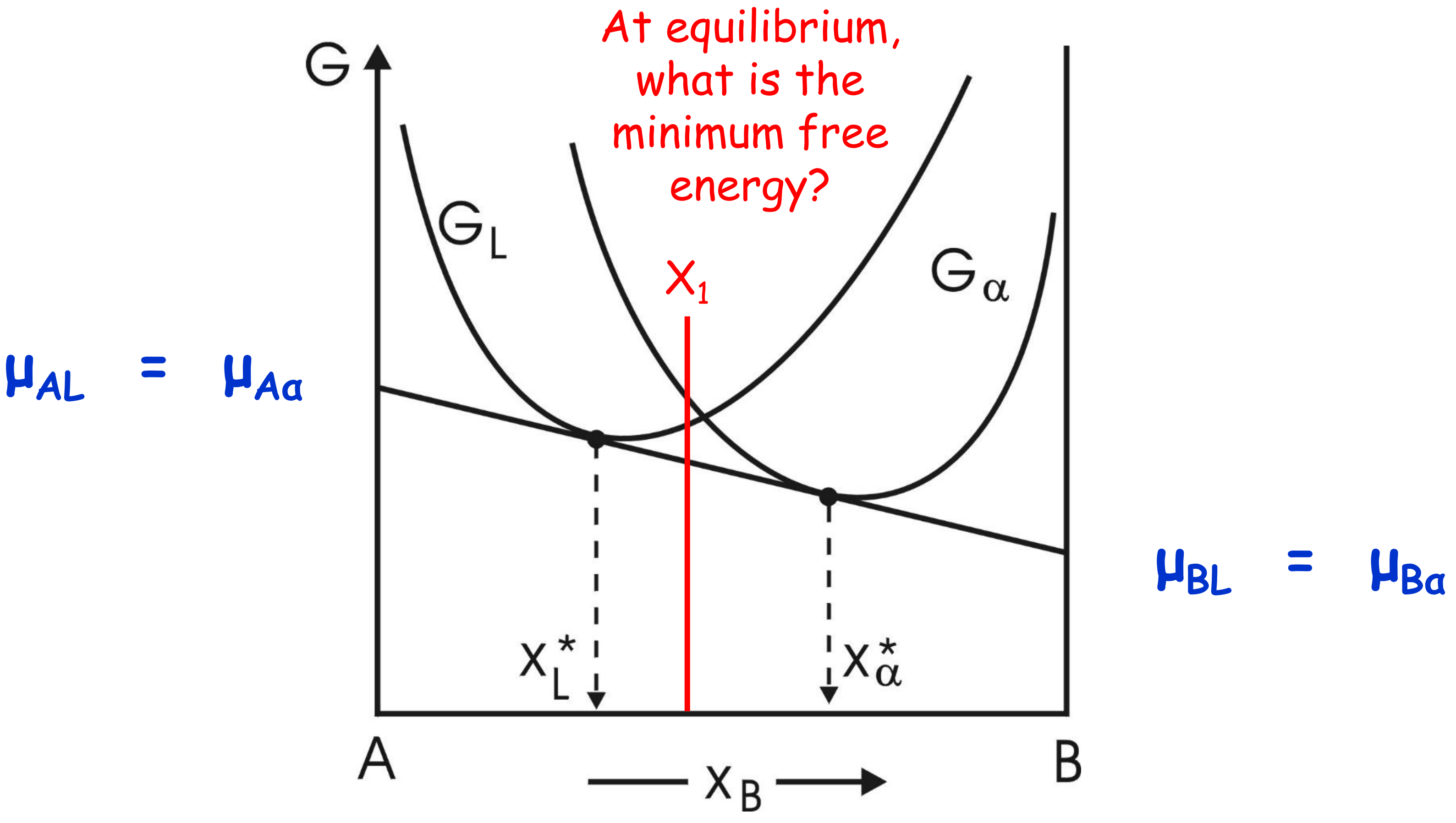
A: 30% A, 70% B

Equilibrium between two phases means:

The chemical potentials of all atoms in all phases are equal!

$$\boxed{\mu_A^{\alpha} = \mu_A^{L} \quad \text{and} \quad \mu_B^{\alpha} = \mu_B^{L}}$$

Situation in G(x)-diagram:



Equilibrium between two phases L and α. Each phase has one G(x)-curve. The common tangent determines the composition of the equilibrium phases.

4. UNDERSTANDING PHASE DIAGRAMS

As materials scientists we must be able to comfortably work with binary phase diagrams.

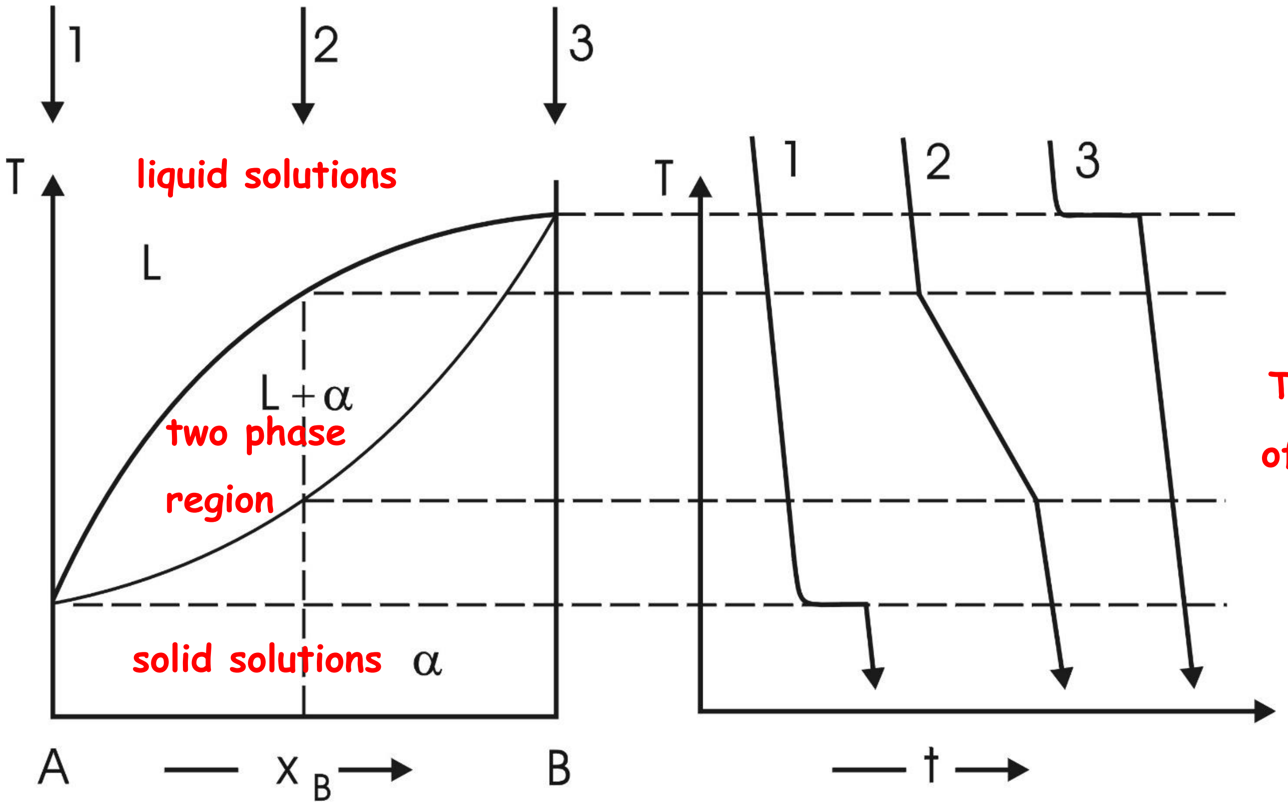
We should also be able to read and understand ternary phase diagrams.

Only then can we appreciate multicomponent systems.

Phase diagrams are equilibrium diagrams ($\Delta G=0$)

We want to be able to interpret phase diagrams on a thermodynamic basis.

A binary system with full solubility in the liquid and in the solid state



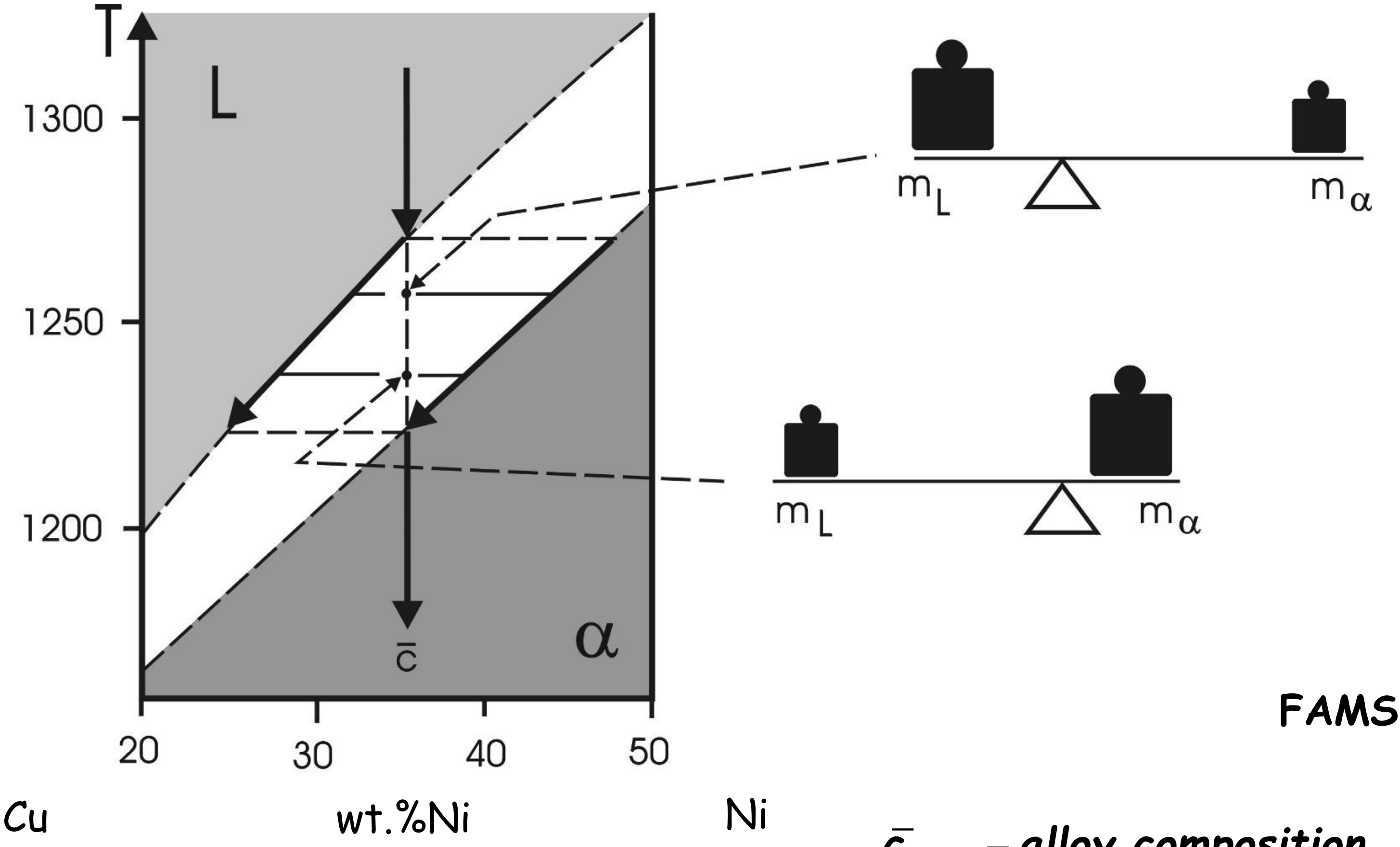
phase diagram

cooling curves

Thermal analysis

of phase diagrams

Cooling through a two phase region: THE LEVER RULE



$$\boxed{m_L \cdot (\bar{c} - c_L) = m_\alpha \cdot (c_\alpha - \bar{c})}$$

$\bar{c}$ – *alloy composition*

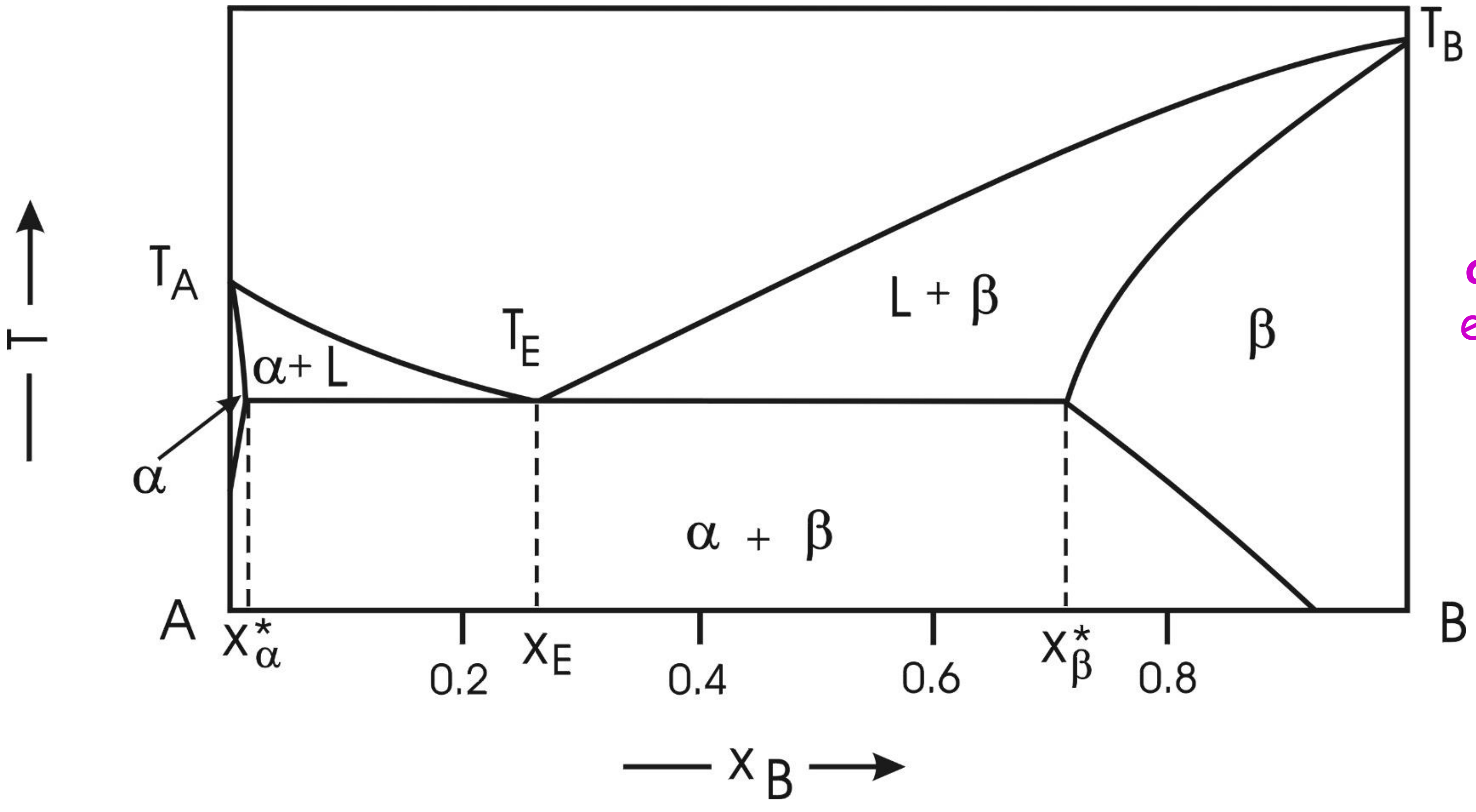
m_L – *mass of liquid phase L*

c_L – *concentration of liquid phase L*

m_α – *mass of solid phase* α

c_α – *concentration of solid phase* α

BINARY EUTECTIC SYSTEM

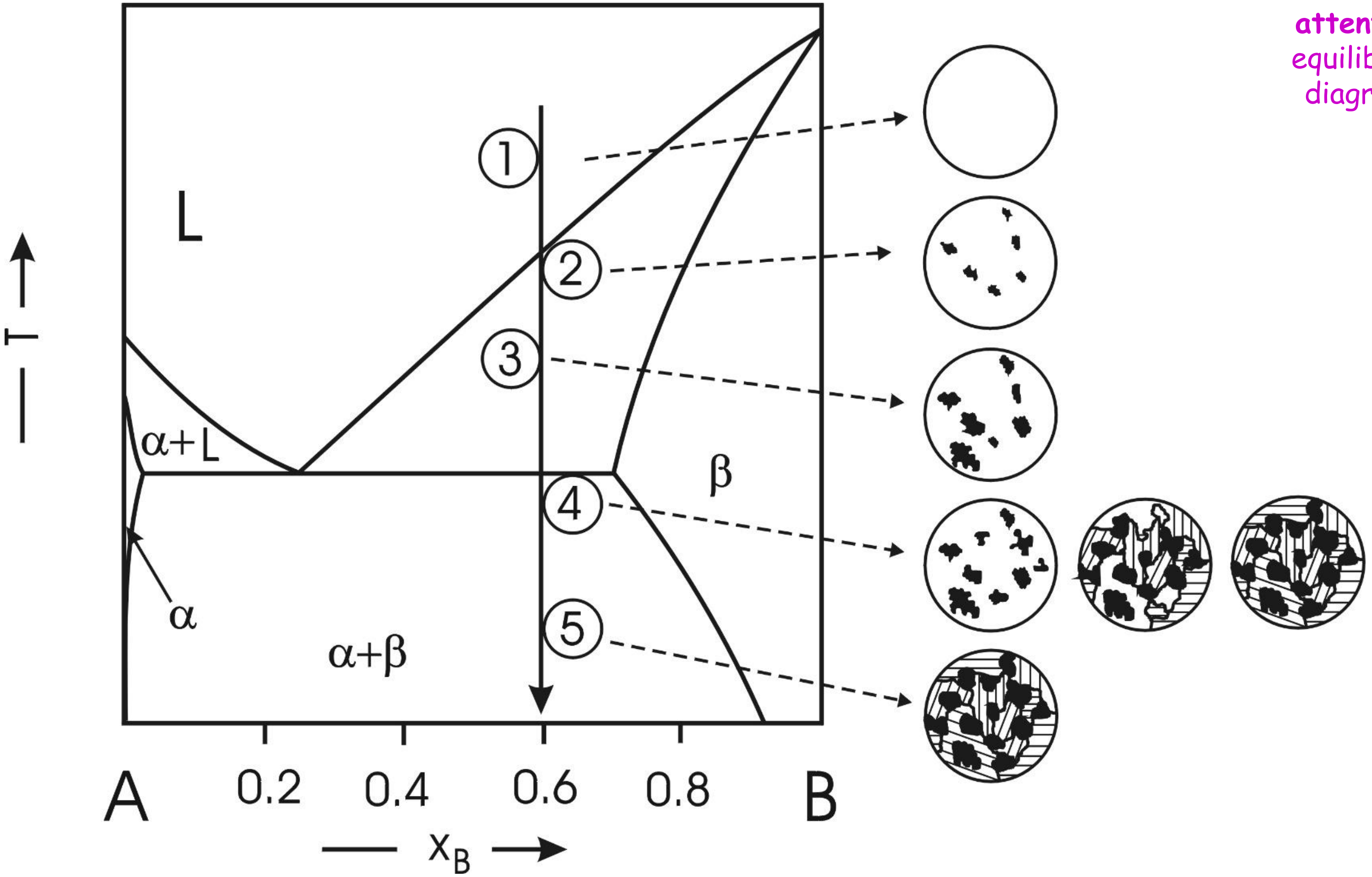


attention:
equilibrium
diagrams

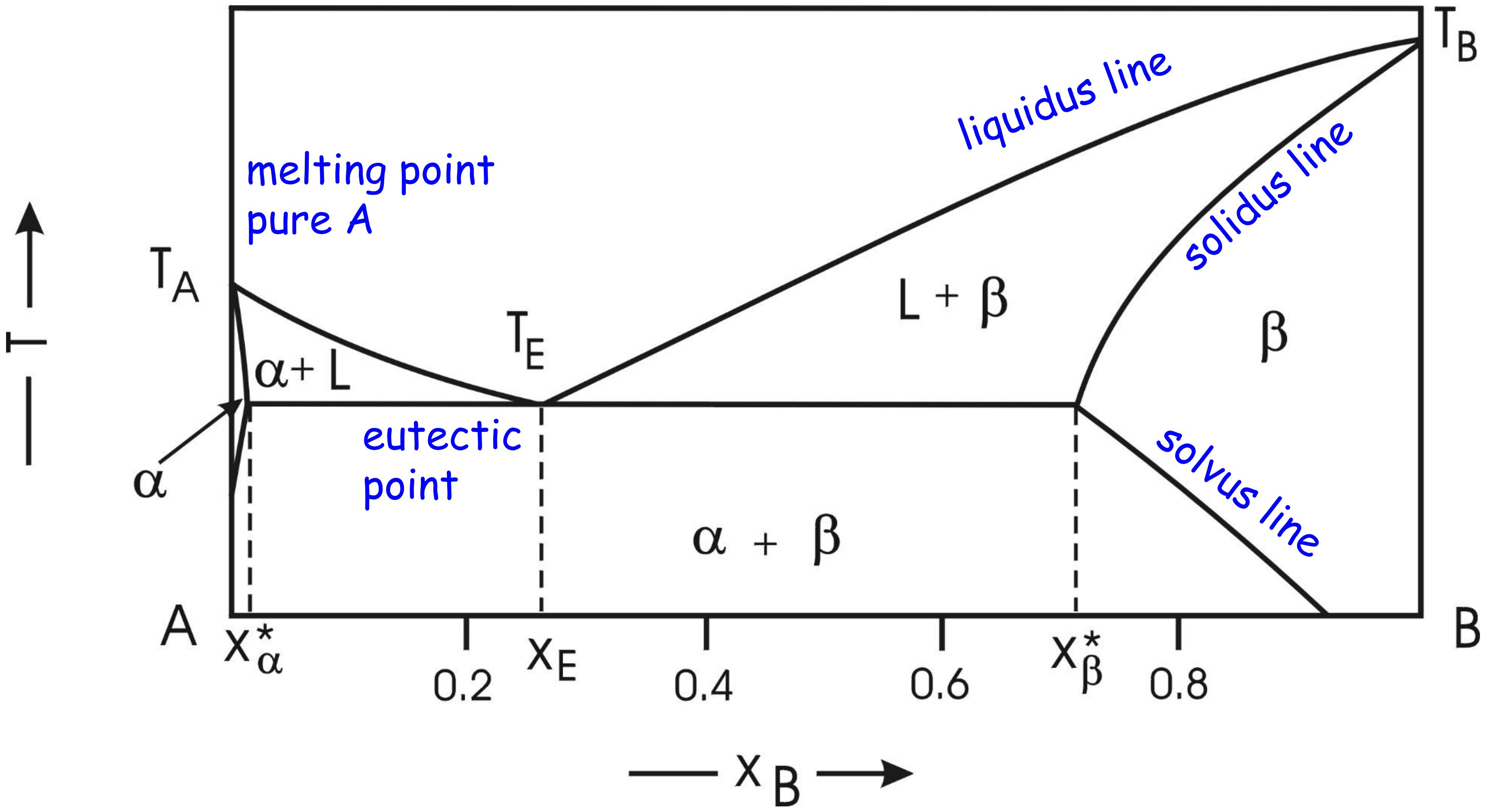
Simple eutectic system

Eutectic reaction:
$L \rightarrow \alpha + \beta$

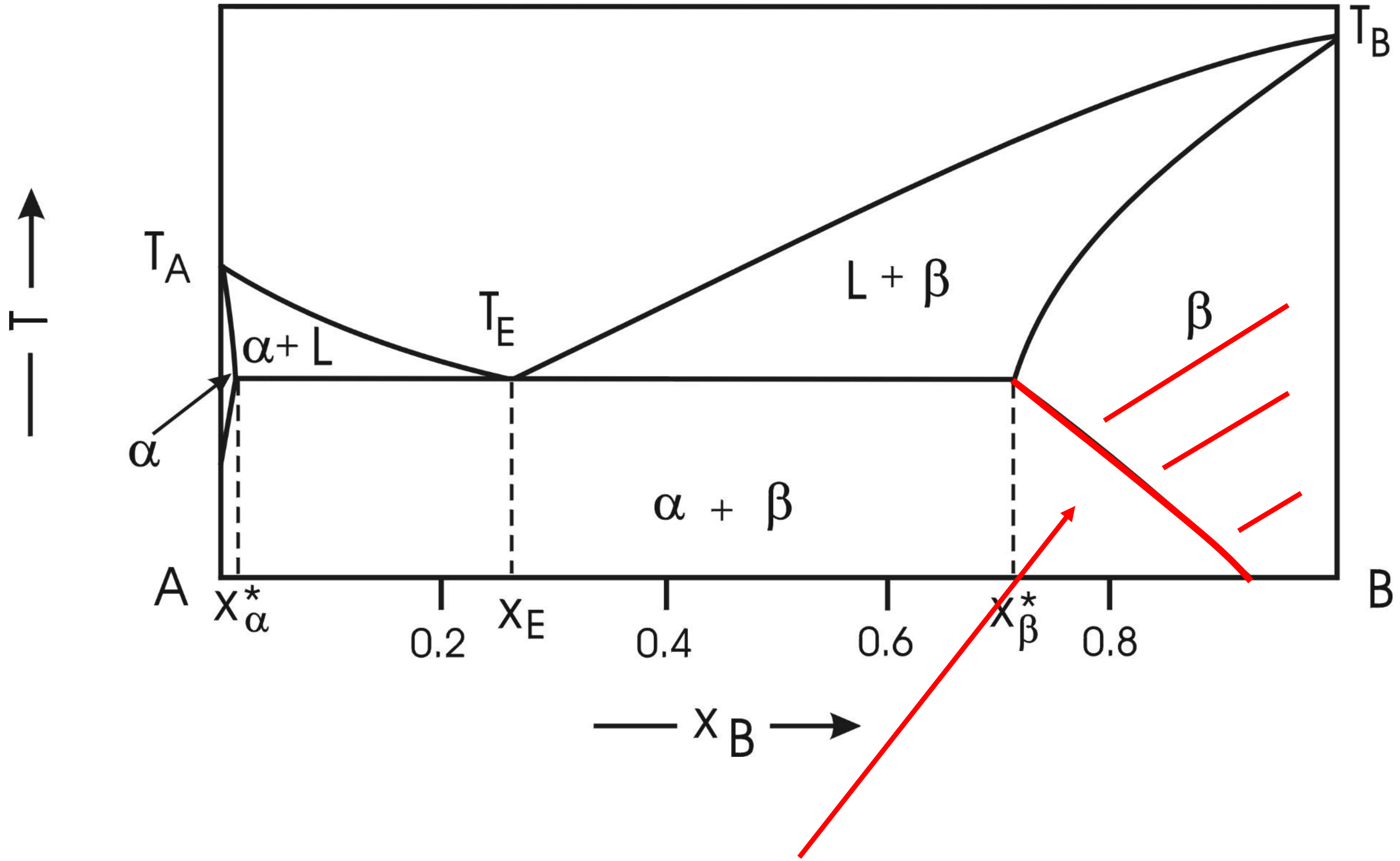
attention:
equilibrium
diagrams



How phase diagrams are used to discuss the evolution of microstructures

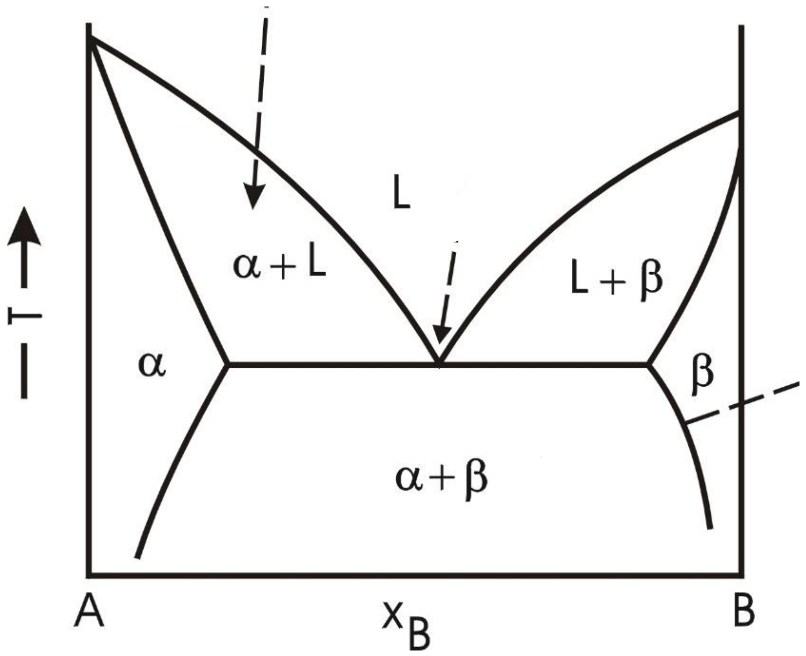


T_B
liquidus line
solidus line
melting point
pure A
T_A
T
L + β
β
T_E
α+ L
eutectic
point
α
α + β
solvus line
A
X*_α
0.2
X_E
0.4
0.6
X*_β
0.8
B
X_B

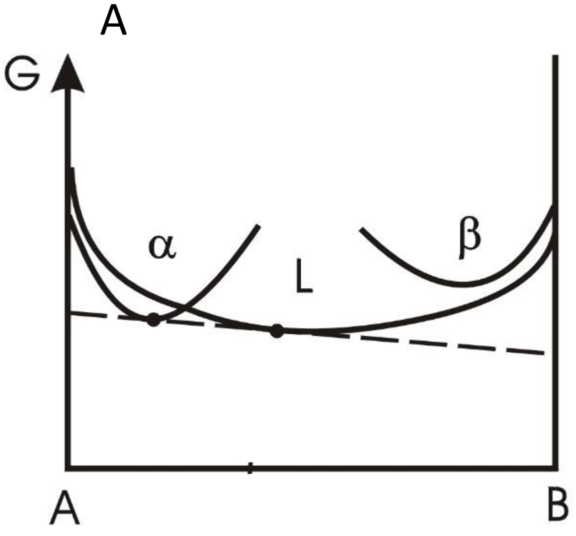


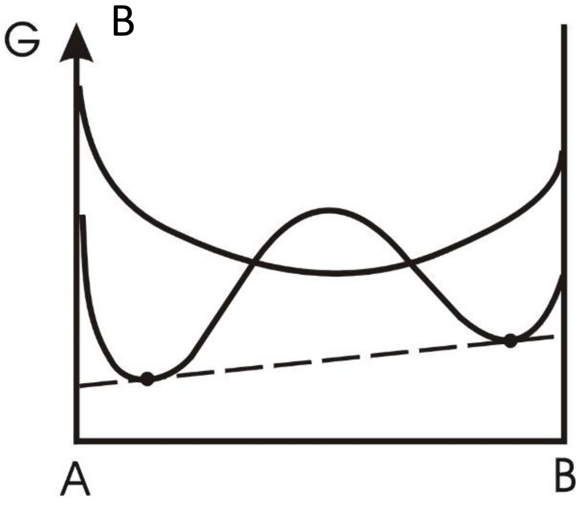
Solubility for A-atoms in β-phase increases with increasing temperature (like sugar in tea).

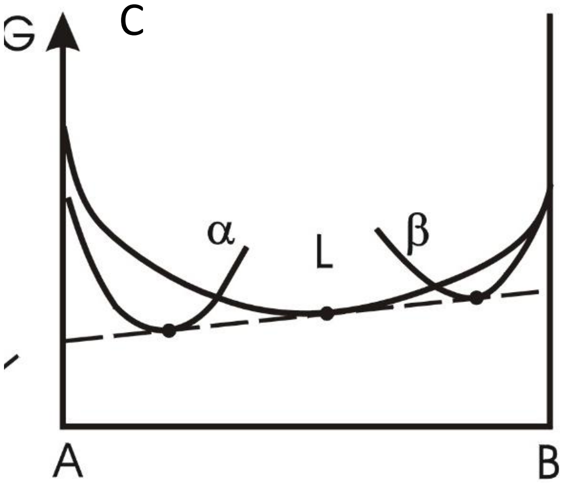
Phase diagram



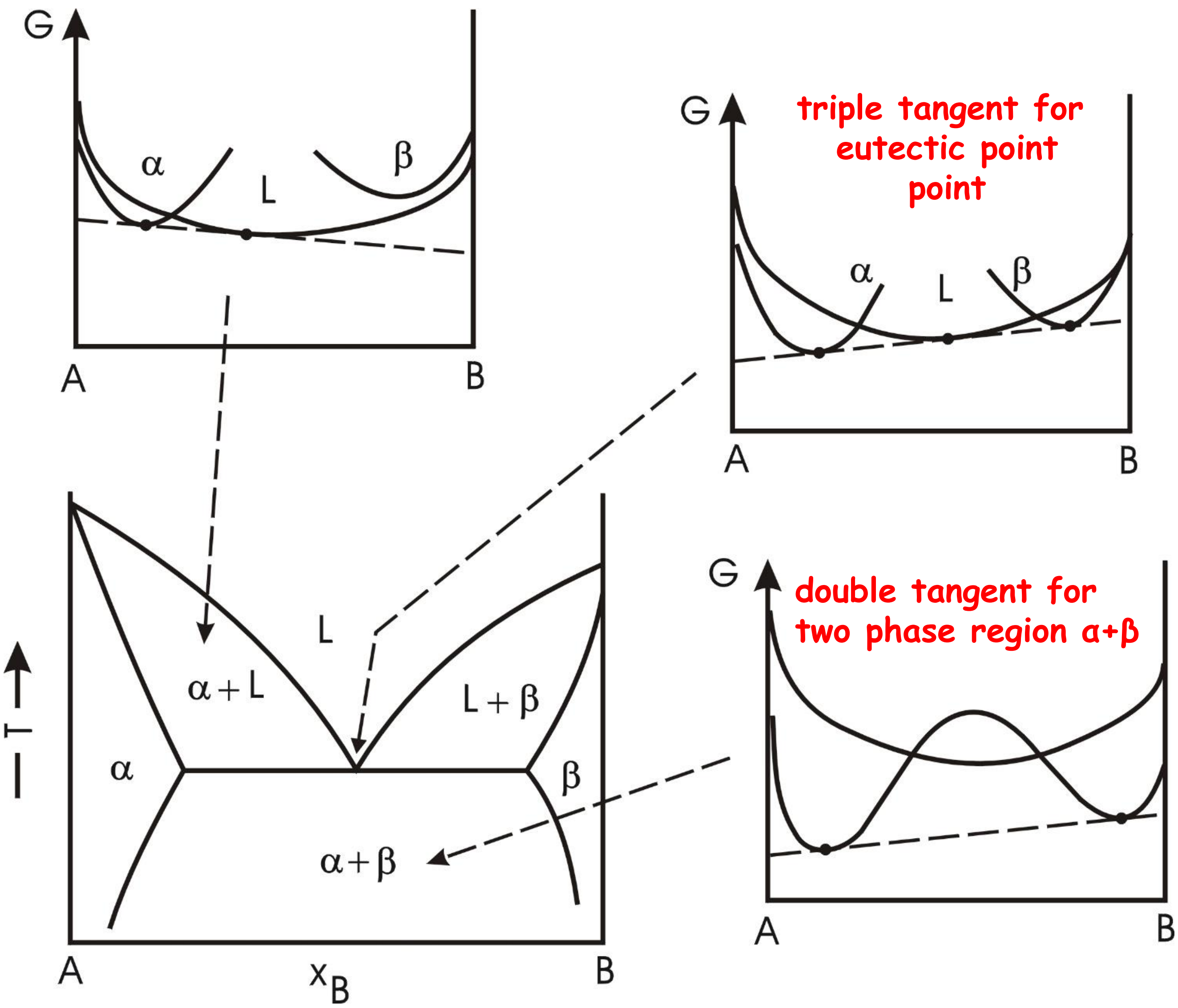
Which part of the phase diagram corresponds to the following G(x) plots?







double tangent for two phase region α+L



triple tangent for
eutectic point
point

double tangent for
two phase region α+β

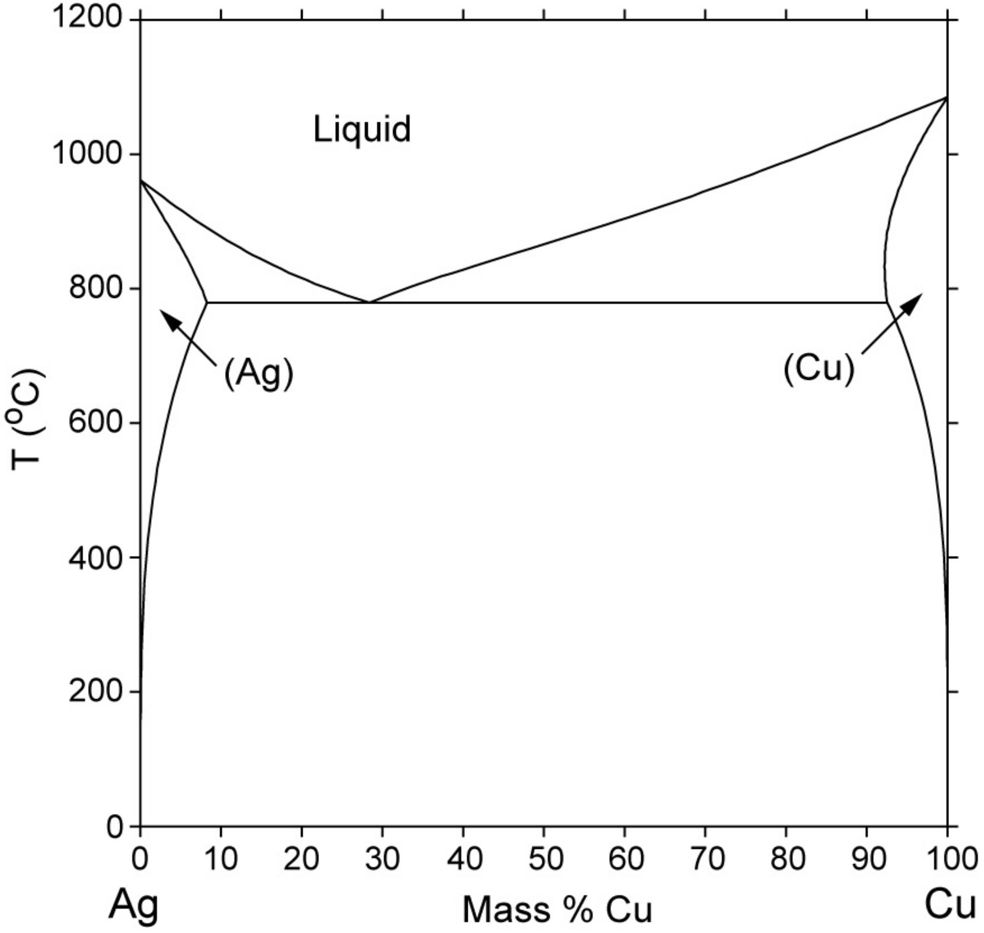
Eutectic phase diagram and G(x)-curves for three conditions in eutectic system.

Eutectica:

On cooling: one high temperature phases decomposes and forms two low temperature phases.

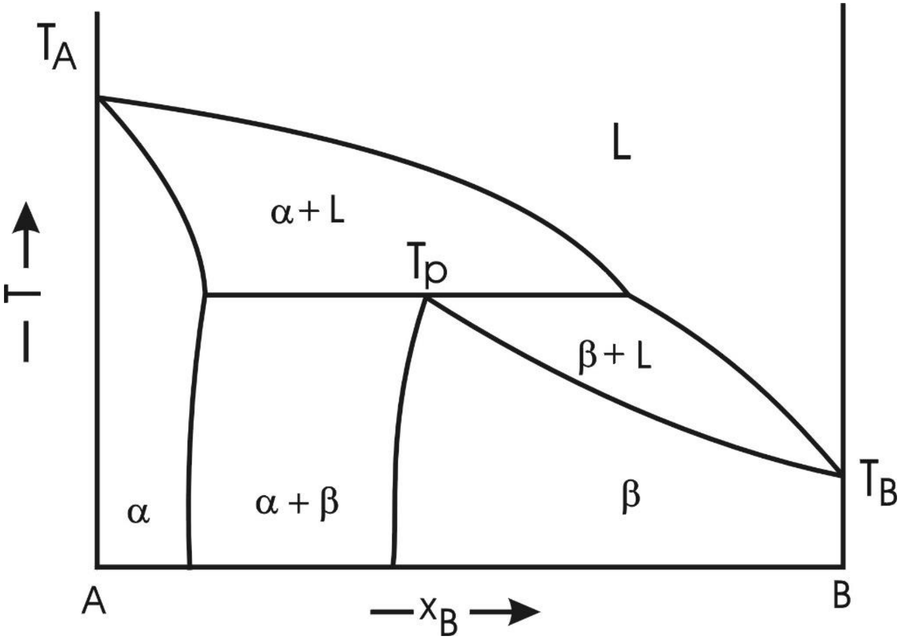
Eutectic microstructures are typically very fine microstructures.

Eutecticum (old greek): The one which is well built. Well built in the sense that at this alloy composition the alloy can melt at the lowest temperature (old times: it was not easy to provide high temperatures). Also in the sense that the melt can reach the lowest temperature (eutectic alloys are good for casting).



Example for a simple eutectic system: Ag-Cu.

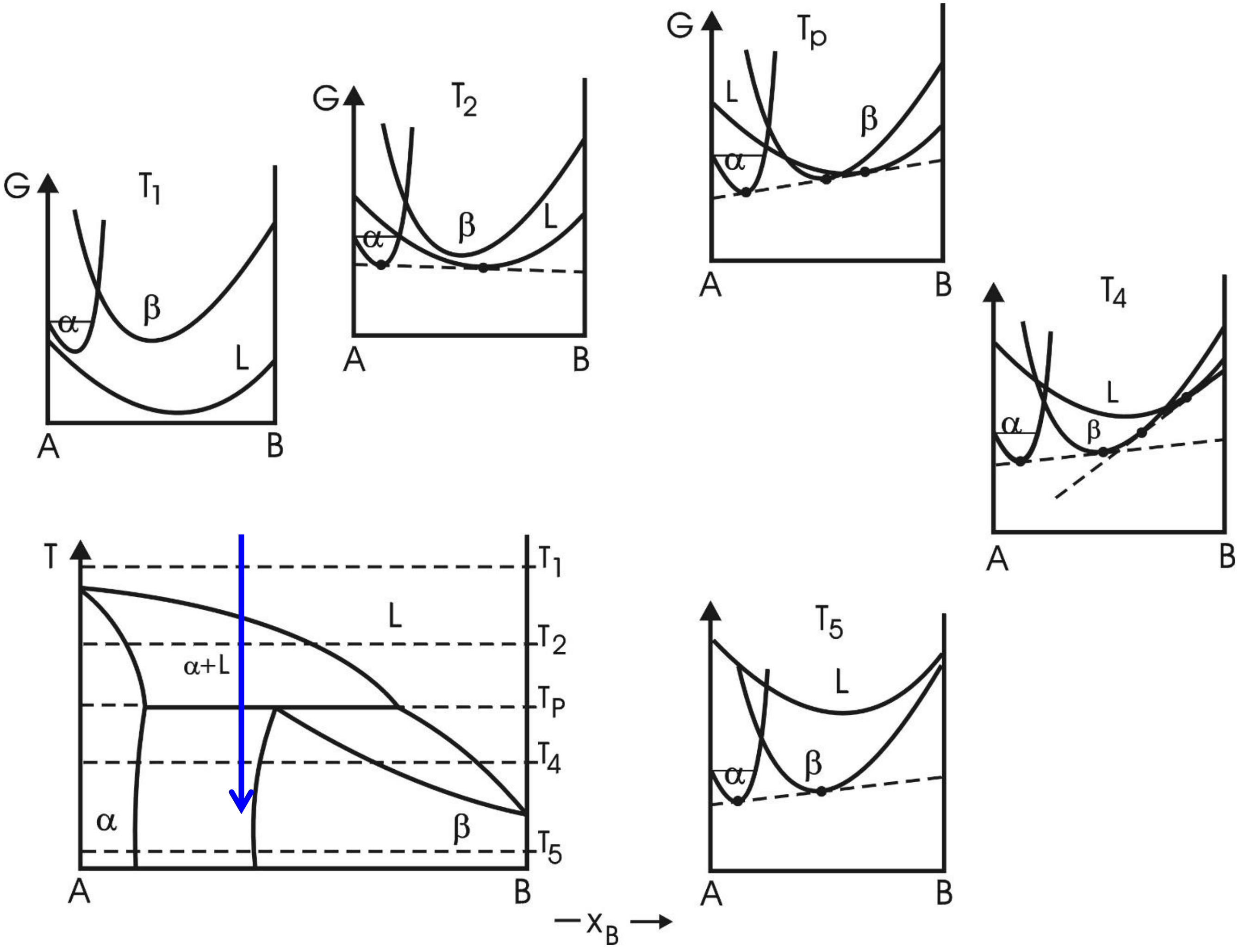
BINARY PERITECTIC SYSTEM



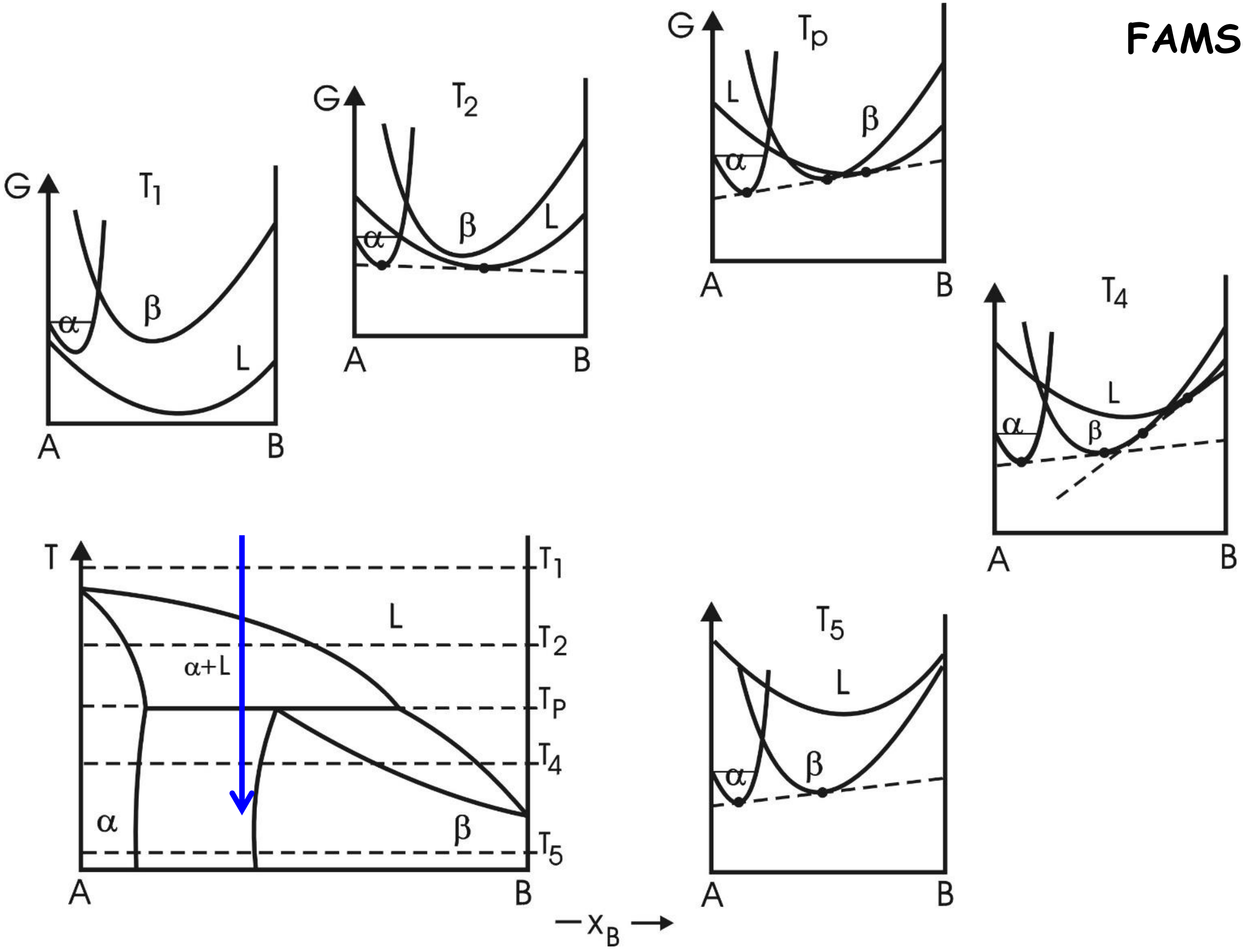
Simple peritectic system

Peritectic reaction:
α + L -> β

attention:
equilibrium diagrams



Peritectic phase diagram and G(x)-curves for the composition indicated by blue vertical arrow.



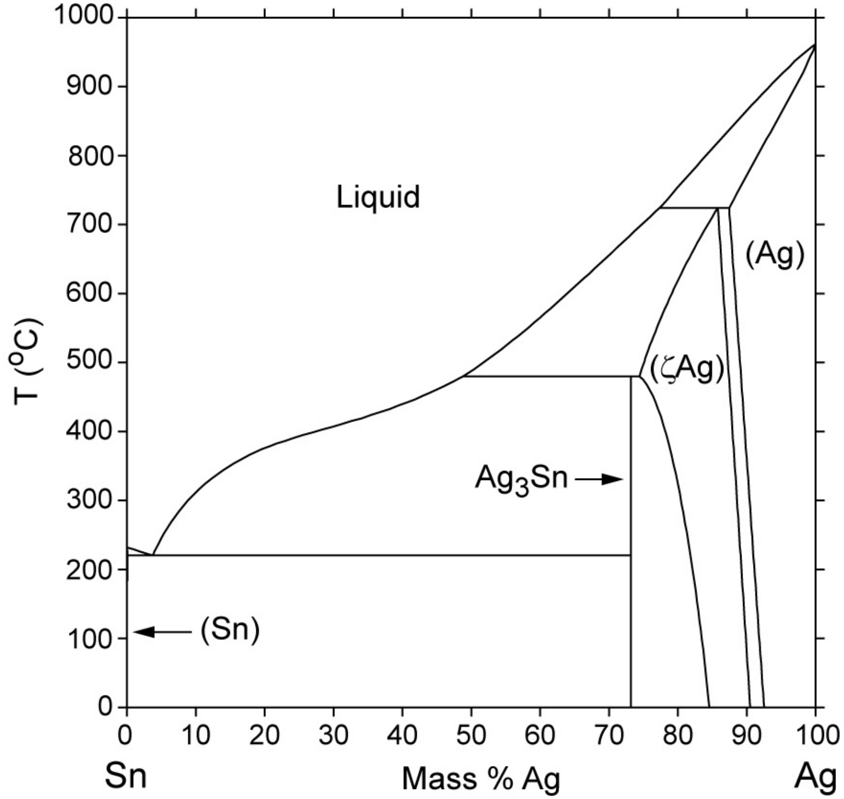
Peritectic phase diagram and G(x)-curves at different temperatures for a composition indicated by blue vertical arrow (schematic).

Peritectica:

We find them in systems, where elements have very different melting points.

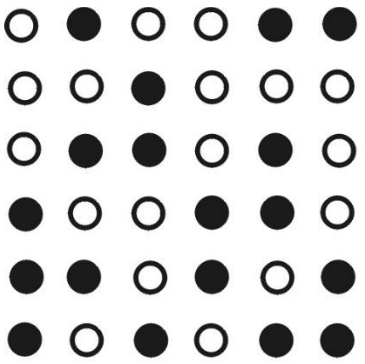
On cooling: two high temperature phases react to form one low temperature phase.

Peritecticum (old greek): The one which is built around. We can understand this when we analyse the reaction.

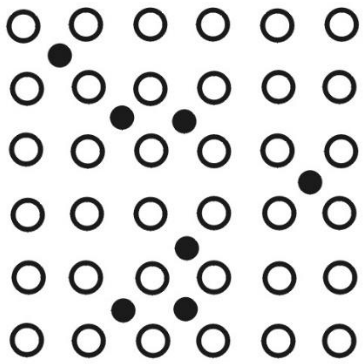


Example for a simple peritectic system: Sn-Ag.

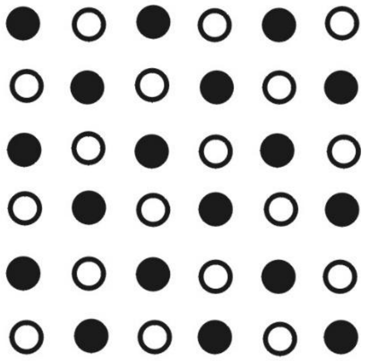
Solid solutions



substitutional
solid solution

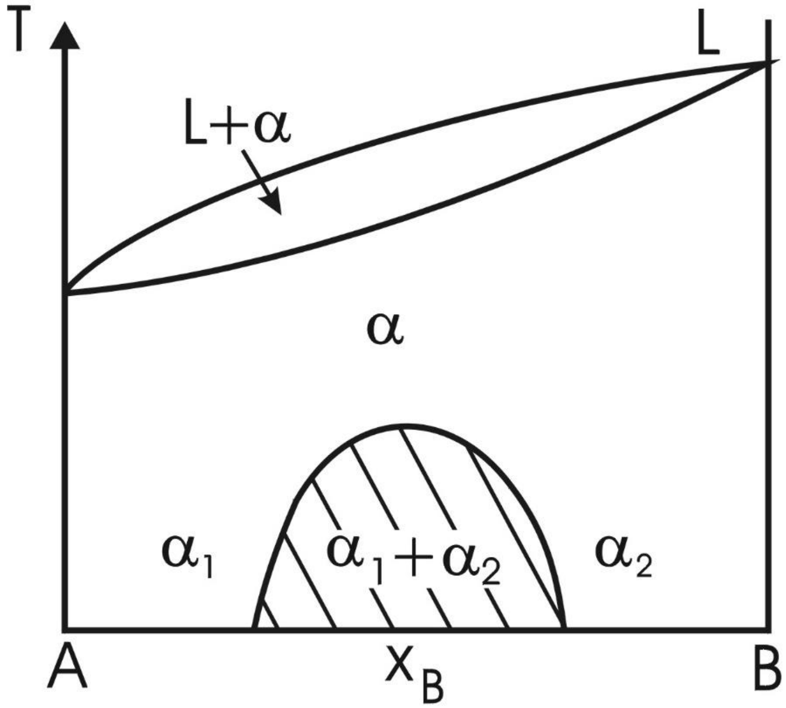


interstitial
solid solution

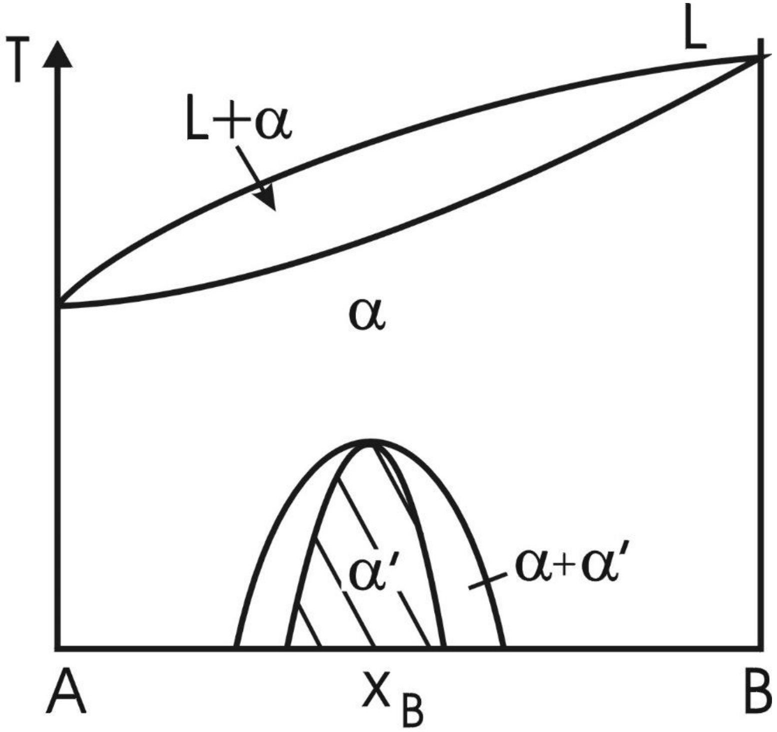


order in 2
component
system
(ordered phase)

Miscibility gaps and ordered phases

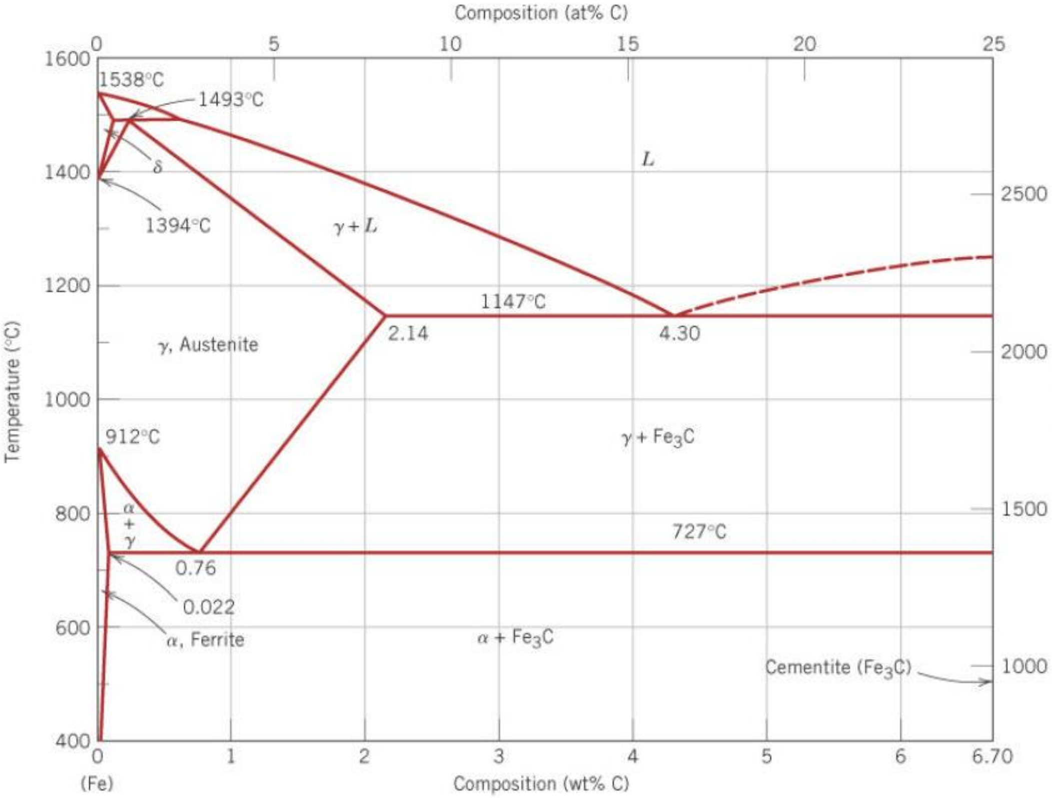


miscibility gap



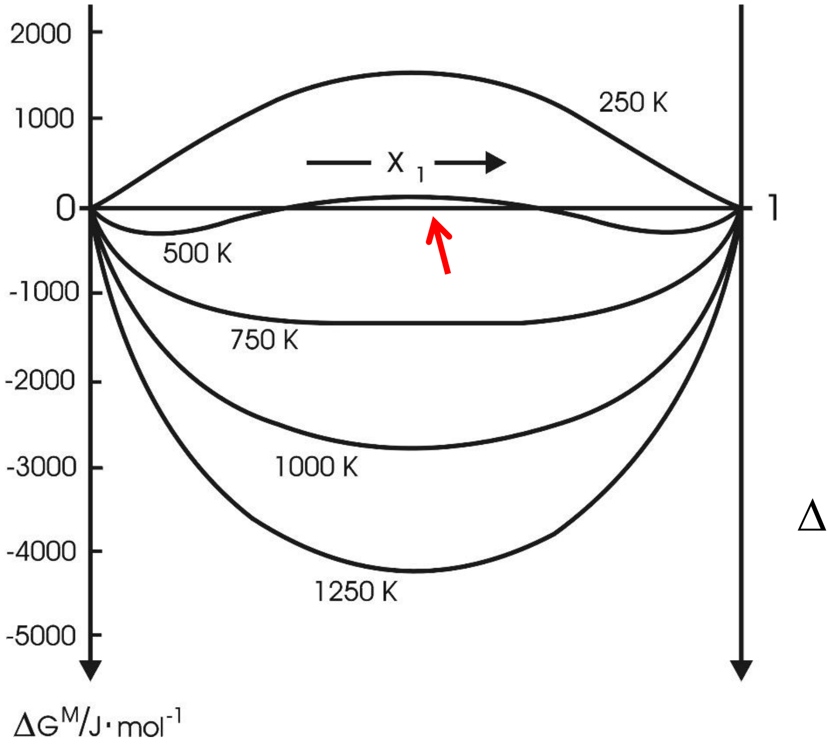
ordered phase
metallic alloy: intermetallic phase

The best known phase diagram in materials science and engineering: Fe-C.



Interesting/important to know:

(a) 2 eutectic reactions and 1 peritectic reaction.
(b) There are differnt irons (α,γ and δ).
(c) The diagram is only interesting up to 25 at.% C, where the compound Fe_3C forms (carbide).
(d) Austenite solves more carbon than ferrite.
(e) c=4.3 wt.% C: cast iron (lowest melting point).
(f) c<2 wt.% C: steel (weldable).



We can use thermodynamics to calculate **miscibility gaps** and the appearance of intermetallic phases.

$$\Delta G^M = z\cdot x_1\cdot x_2\cdot W + R\cdot T\cdot(x_1\ln x_1 + x_2\ln x_2)$$

miscibility gap : $\dfrac{\partial\Delta G^M}{\partial x_1} = 0$ *and* $\dfrac{\partial^2\Delta G^M}{\partial^2 x_1} = 0$

Results:

From $\frac{\partial \Delta G^{M}}{\partial x_{1}} = 0$ and $\frac{\partial^{2} \Delta G^{M}}{\partial^{2} x_{1}} = 0$ we get:

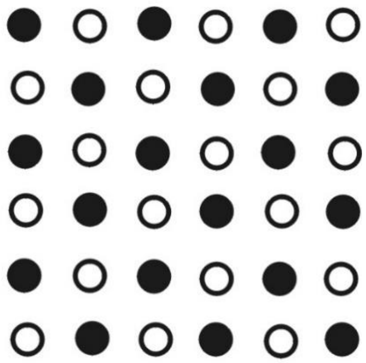
width b of a miscibility gap:

$$\frac{1}{b} \cdot \ln \frac{1 + b}{1 - b} = \frac{z \cdot W}{R \cdot T}$$

Temperature where intermetallic phase forms:

$$T_{IP} = \frac{z \cdot W}{2 \cdot R}$$

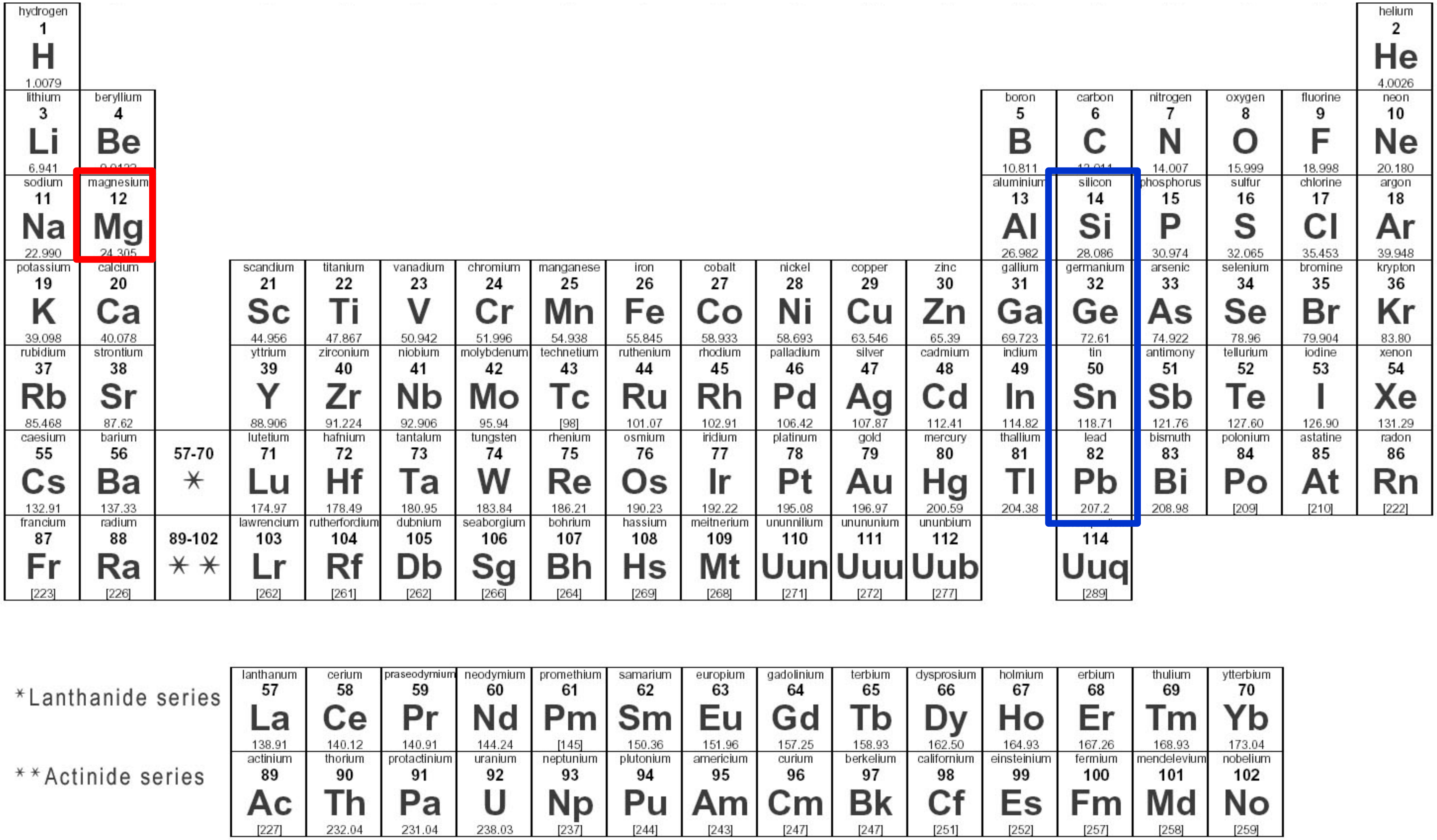
On the appearance of ordered phases (compounds; metallic alloys: intermetallics)



<u>Possibilities (quite common):</u>

- valence electron compounds
- NiAs-compounds
- Hume-Rothery phases
- Laves-Phasen phases

Valence electron compounds:



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		114 Uuq [289]				

* Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* * Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Valence electron compounds

Metals with elements from PSE groups IV, V und VI

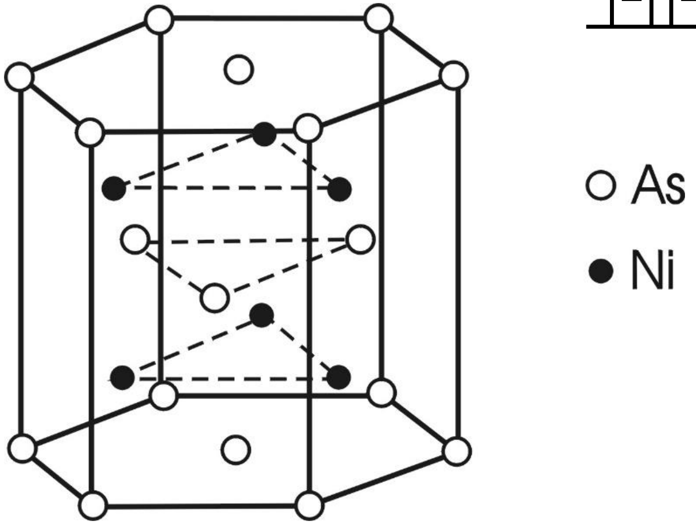
Examples:

Mg_2Si – T_S = 1085°C
Mg_2Ge – T_S= 1115°C
Mg_2Sn – T_S= 778°C
Mg_2Pb – T_S= 550°C

↓ decreasing electronegativity

- valence electron compounds
- NiAs-compounds
- Hume-Rothery phases
- Laves-Phasen phases

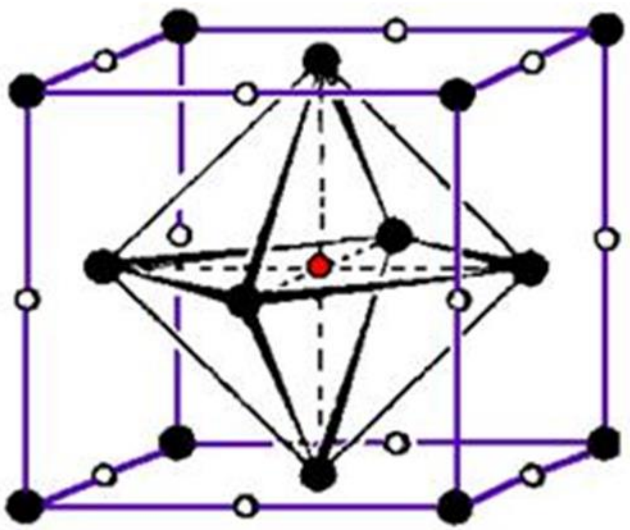
- valence electron compounds
- **NiAs-compounds**
- Hume-Rothery phases
- Laves-Phasen phases



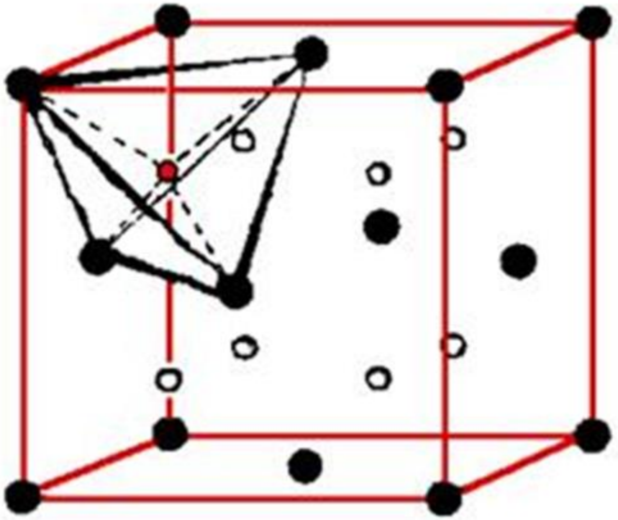
Compounds between: Se, Te, Sn, Sb, As, Bi
with transition metals: Fe, Cr, Co, Ni, Mn

In NiAs, As-atoms have a clolsely packed sublattice.
In NiAs Ni occupies octahedral sites.

Sites in crystals:



octahedral site



tetrahedral site

- valence electron compounds
- NiAs-compounds
- **Hume-Rothery phases**
- Laves-Phasen phases

We get similar crystal lattices for similar valence electron concentrations per atom of compound (VEC)

VEC = Number of electrons per atom of compound

VEC-CuBe: $(1 \cdot 1 - 1 \cdot 2)/2 = 3/2$; VEC-$CuZn_3$: $(1\ (1 \cdot 1 - 3 \cdot 2)/4 = 7/4$

VEC = 3/2: bcc Examples: CuBe, CuZn, Cu_3Al, Cu_5Sn

VEC = 7/4: hex Examples: $CuZn_3$, Cu_3Sn, $AgZn_3$

- valence electron compounds
- NiAs-compounds
- Hume-Rothery phases
- **Laves-Phasen phases**

Nature of compound governed by ratio of atom radii of elements.

E.g. ratio of atom radii 1 : 1,225 -> AB_2-Compounds

More closely packed (e.g. 0,71) as bcc (e.g. 0,682).

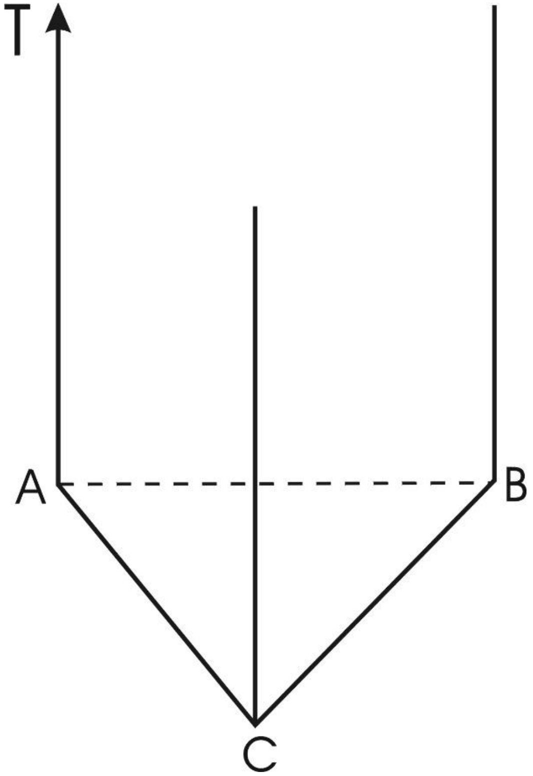
Famous example: Fe_2Mo in steels.

In phase diagrams we find compounds (metallic alloys: intermetallic phases).

We have discussed a few well known type of phases.

Research on compounds and intermetallic phases is an important part of modern structural materials science.

5. TERNARY PHASE DIAGRAMS

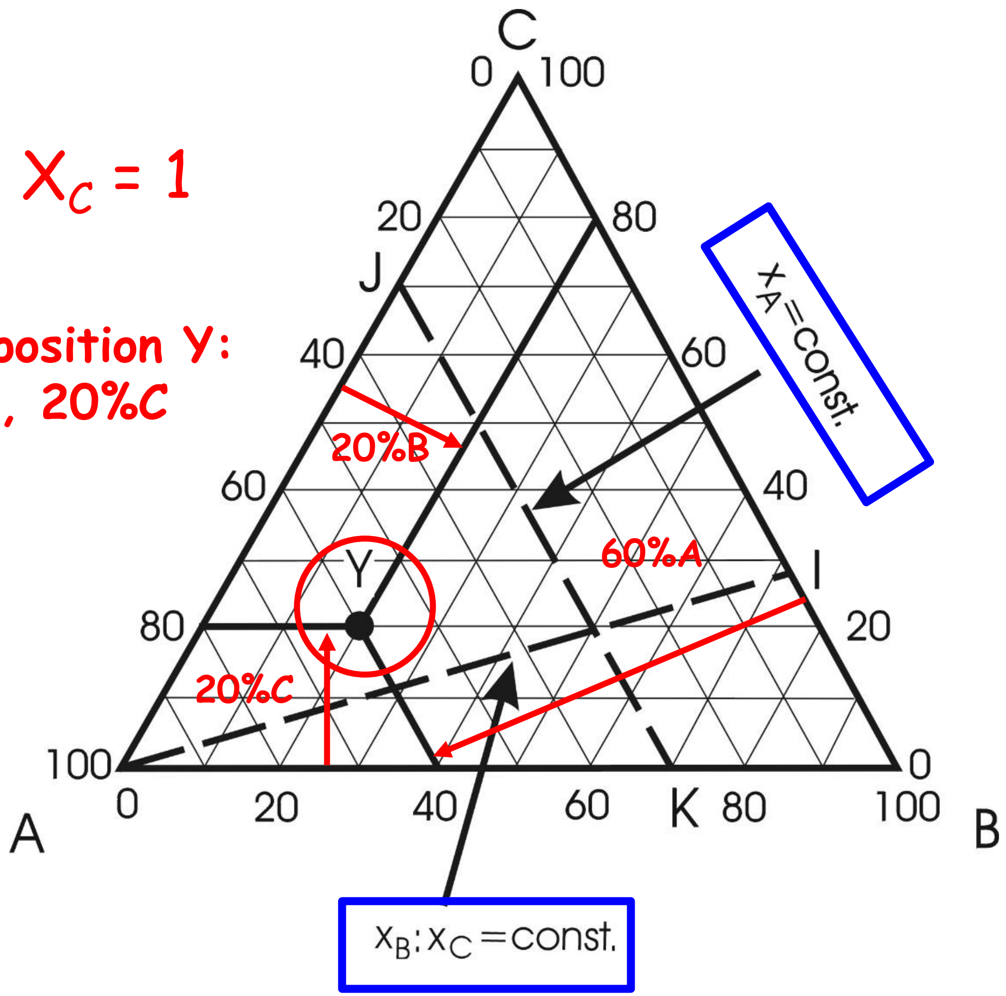


$$X_A + X_B + X_C = 1$$

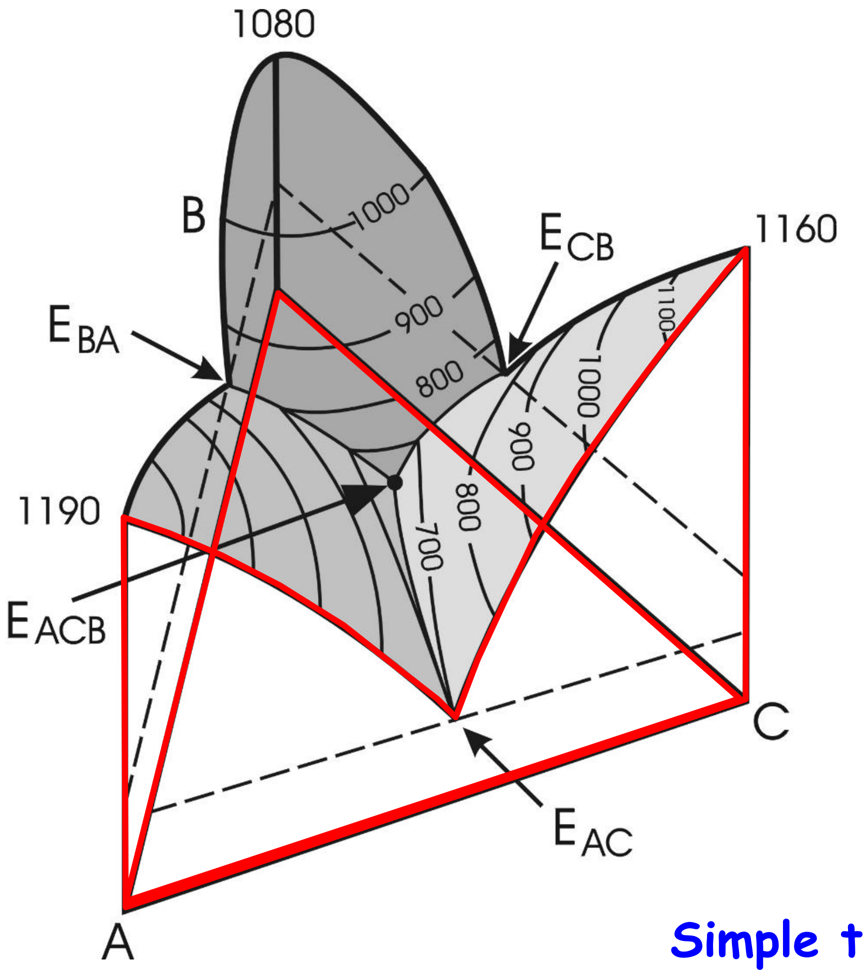
A 3D frame for a ternary phase diagram.

$X_A + X_B + X_C = 1$

Ternary composition Y:
60%A, 20%B, 20%C



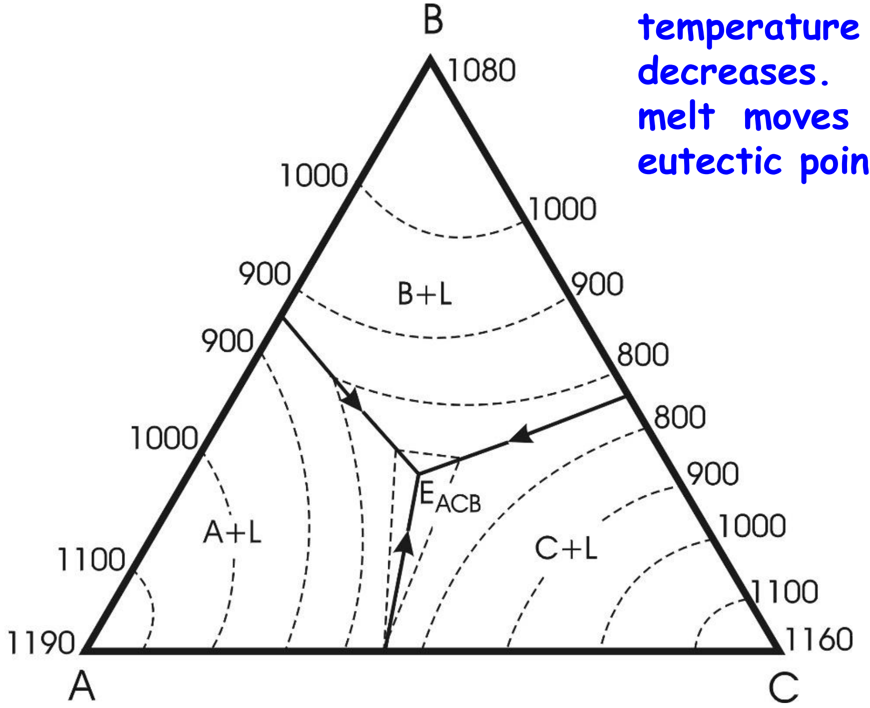
Concentration triangle



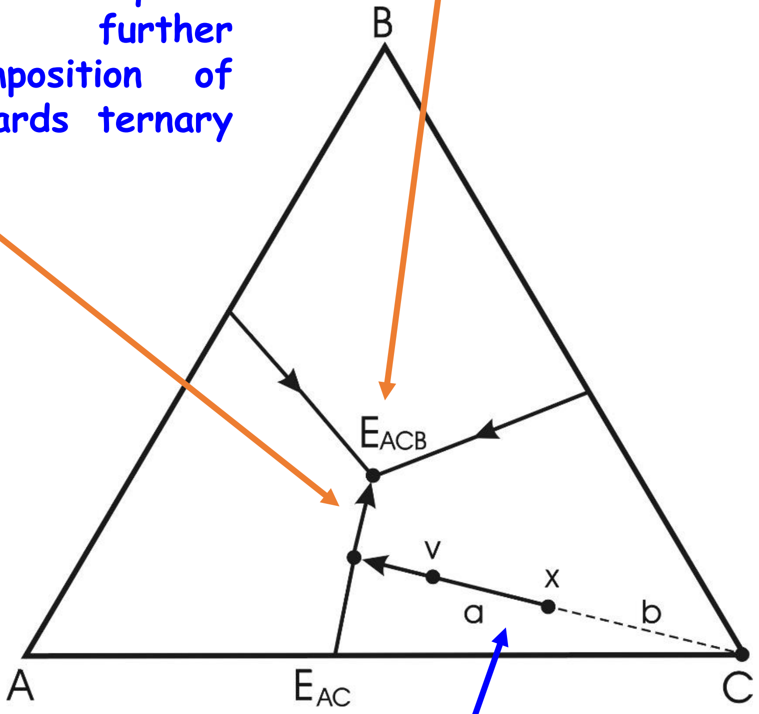
Simple ternary eutecticum.
On each side: a binary eutecticum.

Third: eutectic solidification
L -> A + B + C

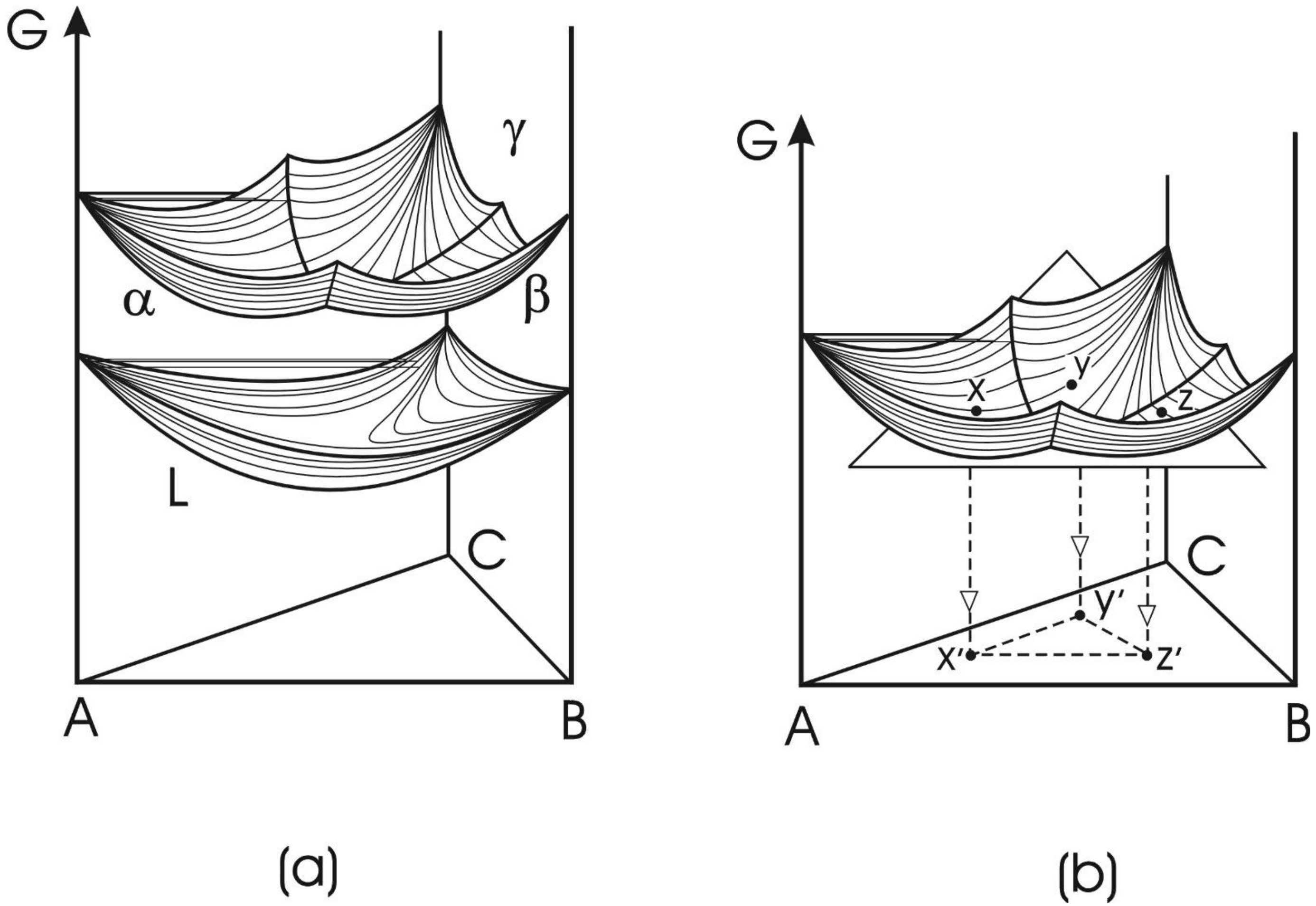
Second: C and A crystallize from melt. Liquidus temperature further decreases. Composition of melt moves towards ternary eutectic point.



projection



First: C crystallizes from the melt. Liquidus temperature decreases. Composition of melt moves towards eutectic groove between E_{AC} and E_{ACB}.



G(X)-planes. (a) Liquid is stable. (b) Equilibrium composition at ternary eutectic point.

6. HIGH ENTROPY ALLOYS

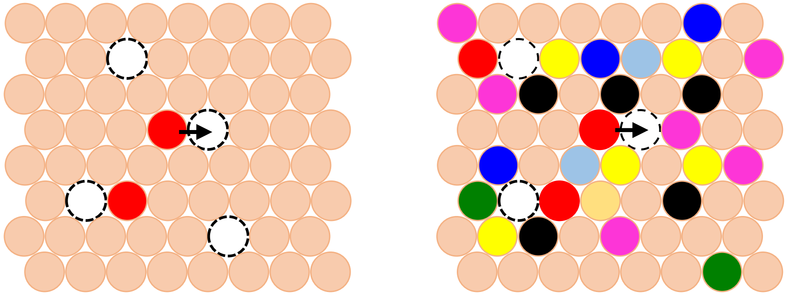
Recently a new class of **equiatomic** alloys has been proposed – no "base" element (e.g. $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$)

- Yeh et al. Adv. Eng. Mater. (2004)
- Cantor et al. Mater. Sci. Eng. A (2004)

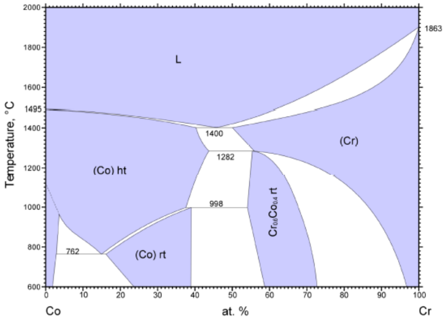
These materials are referred to as high entropy alloys. Today a hot research topic. Here: some background.

Configurational entropy is at maxima → if entropy is dominant contribution to free energy, it becomes to 'stablise' a multiple component solution → single phase.

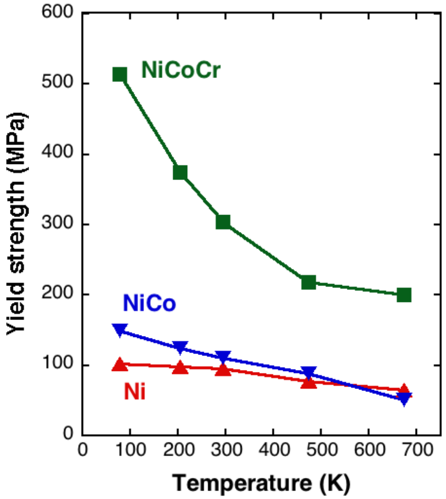
Why are high entropy alloys interesting?



(1) Diffusion behavior



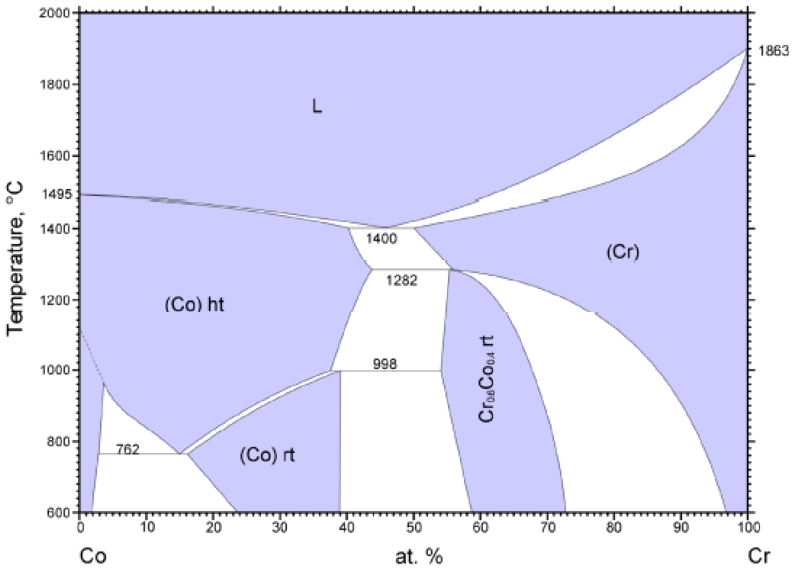
(2) Phase stability

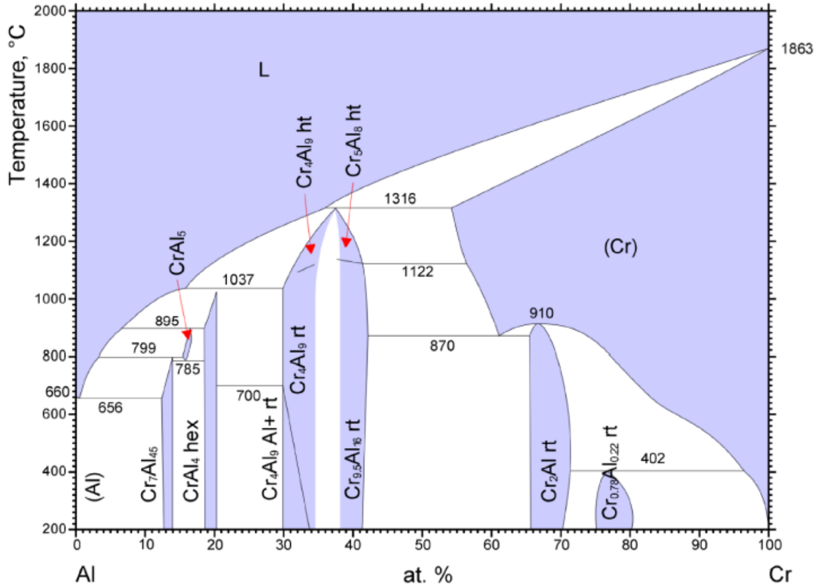


(3) Solid solution strengthening

Three aspects of compositional complexity.

Often: Solid solutions typically form at the ends of phase diagrams while intermetallic compounds are found near the centers





Two tendencies:

(1) Strong heat of formation of intermetallics drives phase separation.
(2) Entropy of mixture promotes single phase solid solutions.

(1)

$$2Cr + Al = Cr_2Al$$

$$\Delta G_f = \Delta H_f - T \cdot \Delta S_f$$

(2)

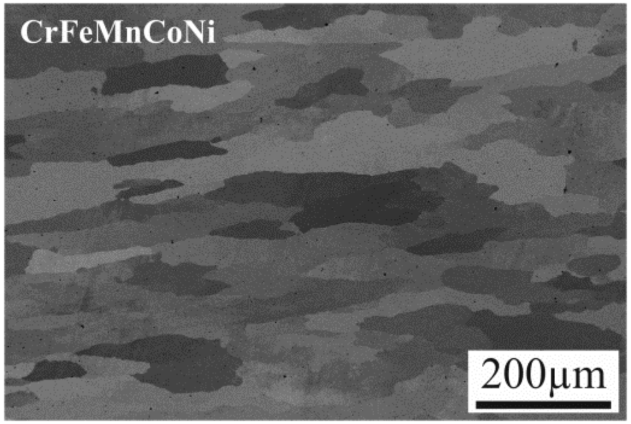
$$Cr + Al = (Cr,Al)_{solution}$$

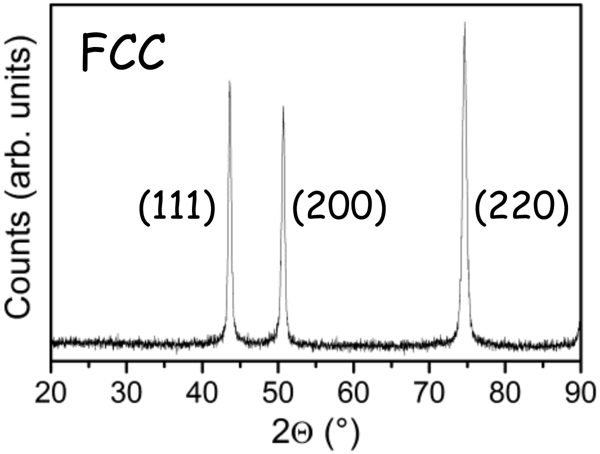
$$\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix}$$

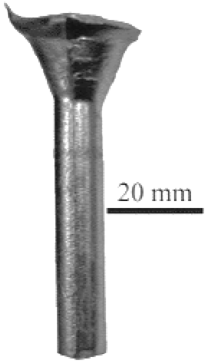
High entropy alloys: multi-component alloys are single phase !

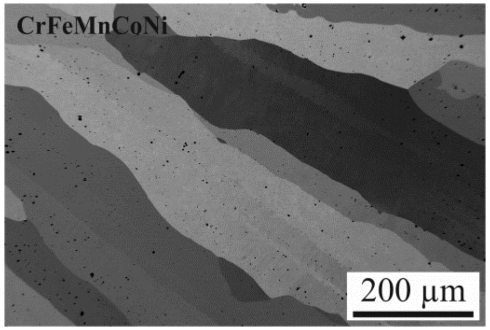
Example:
CrMnFeCoNi

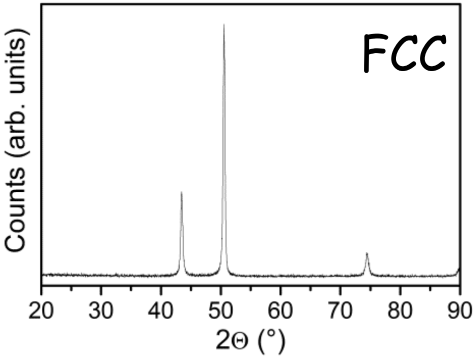
As-cast

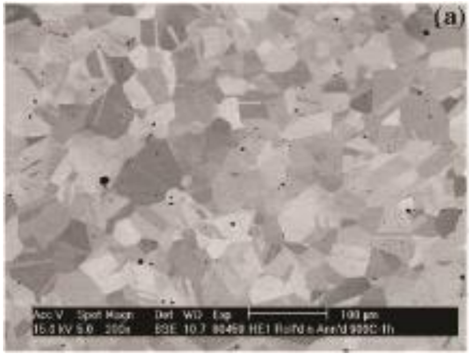












Homogenized at 1000°C for 72 h

Hot rolled at 1000°C

Otto, Yang, Bei, George, Acta Mater. (2013)

Hume-Rothery rules for solid solubility:

- Similar atomic size (difference < 15%)
- Similar crystal structure
- Similar chemical valence
- Similar electronegativity

Atoms of HEA must have similar properties!

Second: Configurational entropy may stabilize solid solutions

Yeh et al. *Adv. Eng. Mater.* 6 299 (2004)

$\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix}$ ⟷ $\Delta G_f = \Delta H_f - T \cdot \Delta S_f$

$$\Delta S_{mix}^{ideal} = -R \sum_{i}^{n} x_i \ln x_i \qquad \sum_{i}^{n} x_i = 1$$

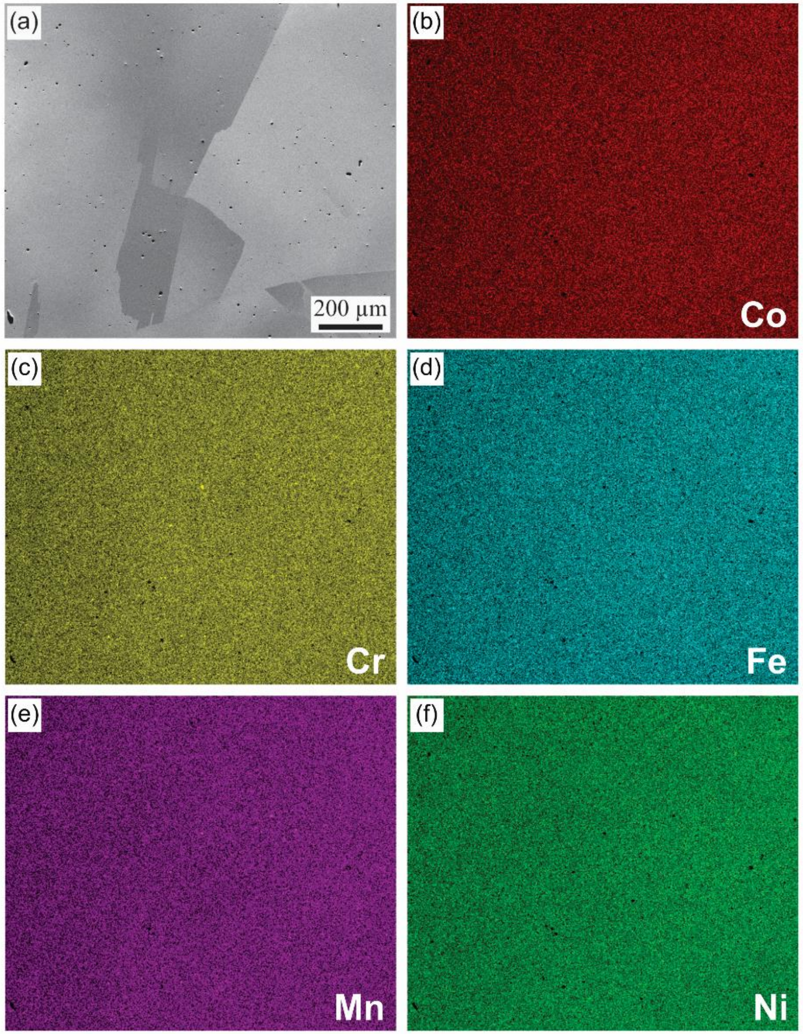
$$\Delta S_{mix} \rightarrow \max .$$

when n is large, and $x_1 \approx x_2 \approx x_3 .... \approx x_i$

For equiatomic alloys: $\Delta S_{mix} = R \ln n$

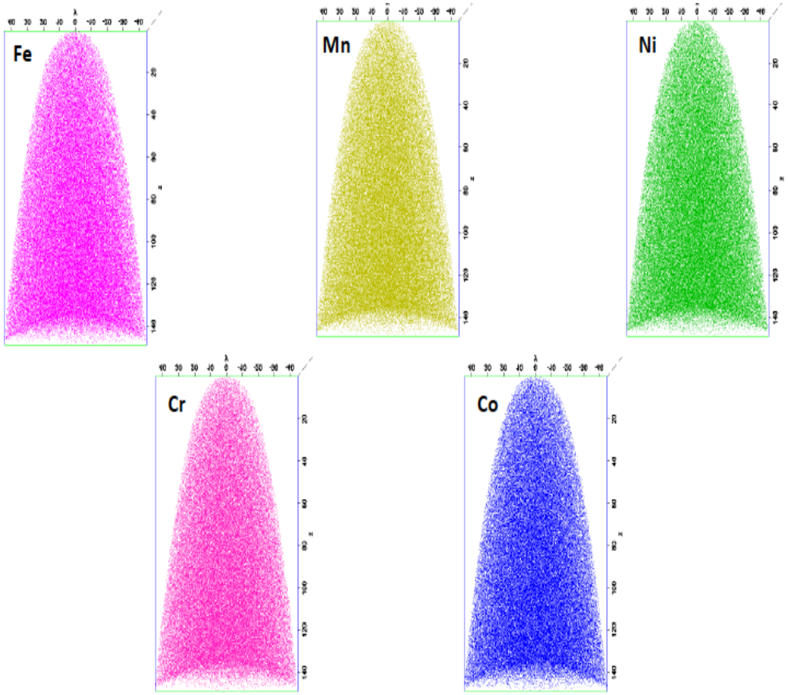
HEAs: equiatomic with $n \geq 5$; $\Delta S_{mix} \geq 1.6 \cdot R$

Single-phase homogeneous microstructure after 48 h at 1200 °C



SEM/EDX results

CrMnFeCoNi

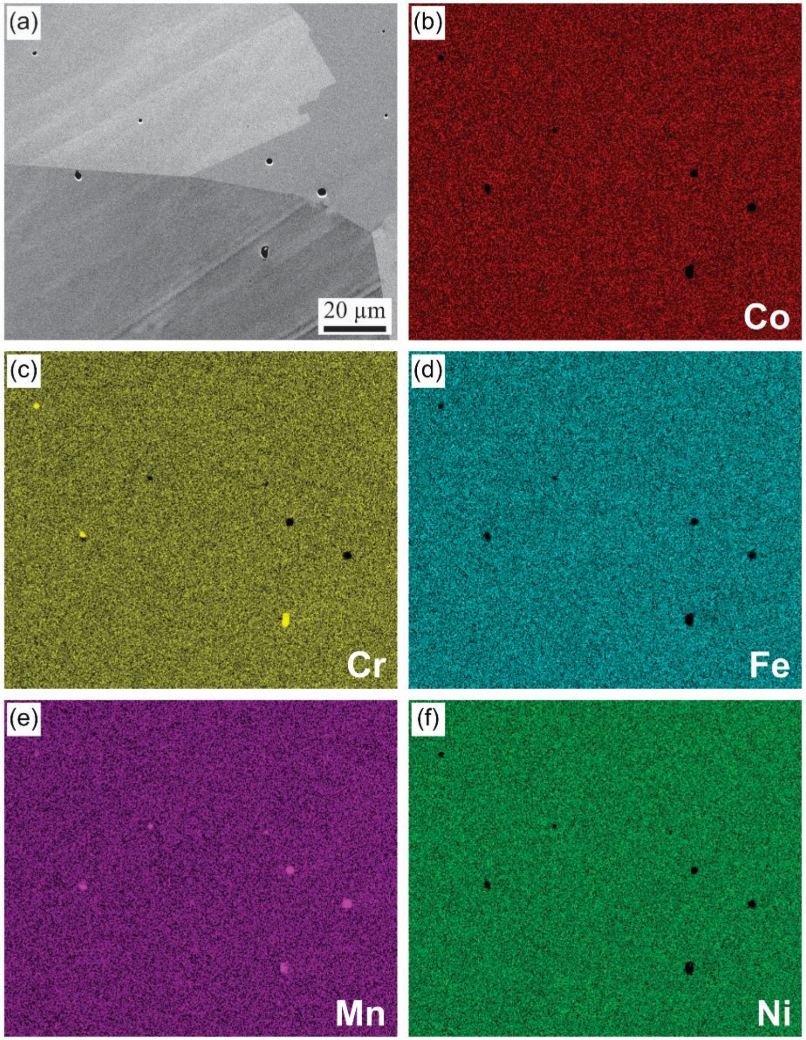


APT results

Otto et al, Acta Mater. (2016)

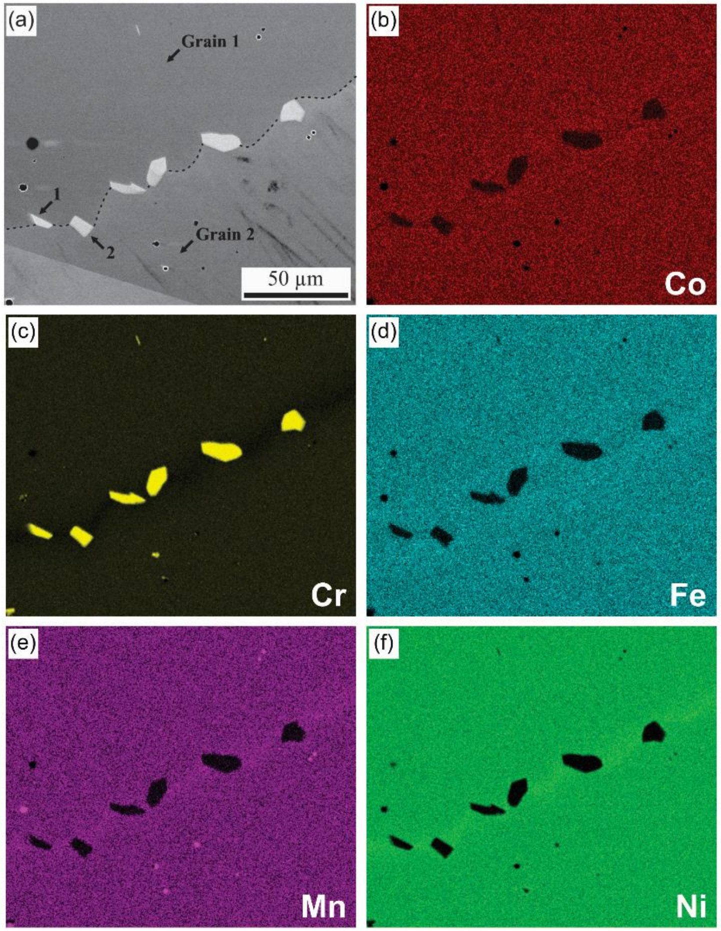
Single-phase homogeneous microstructure after 500 days at 900 °C

SEM/EDX results

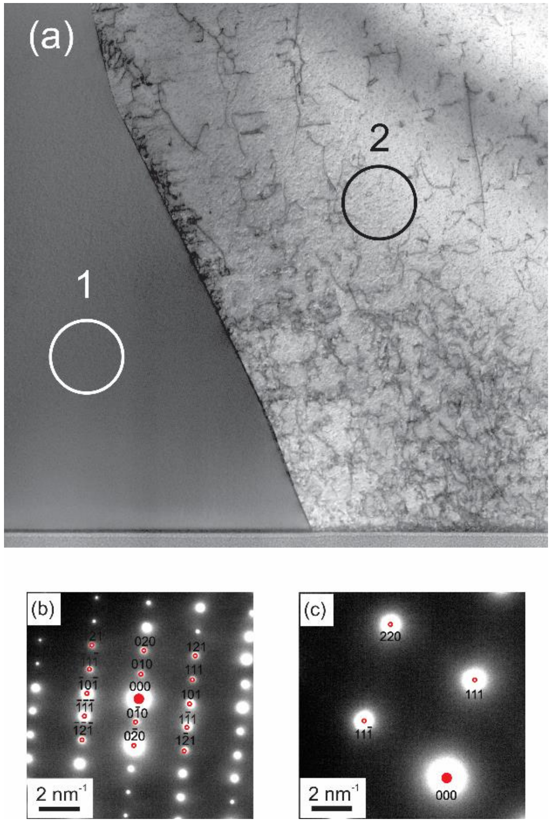


Otto et al, Acta Mater. (2016)

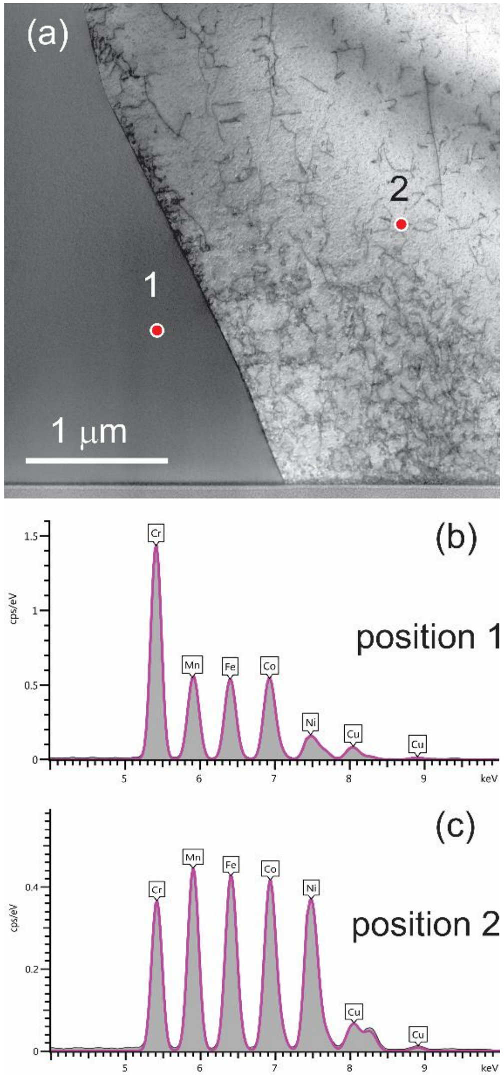
Decomposition into Cr-rich phase after 500 days at 700 °C



SEM-EDX



TEM-SAD

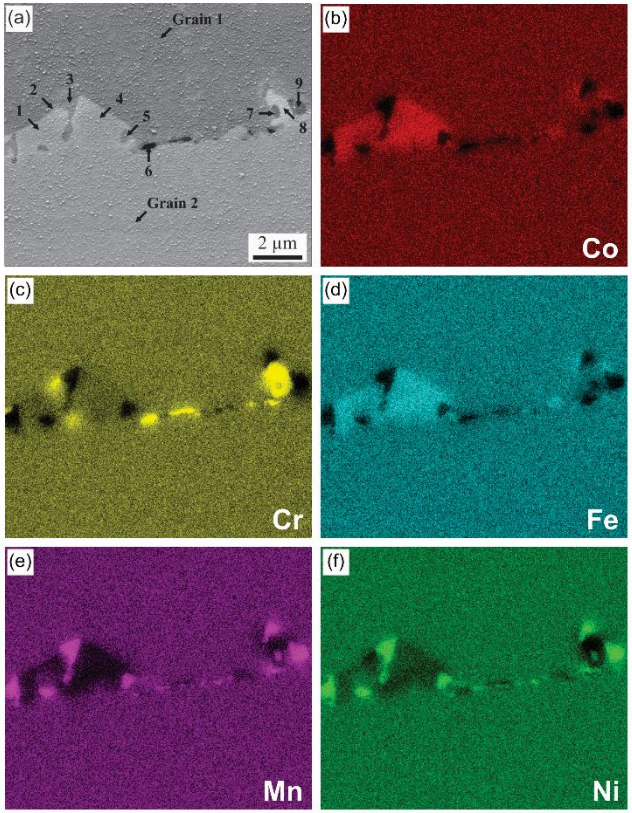


TEM-EDX

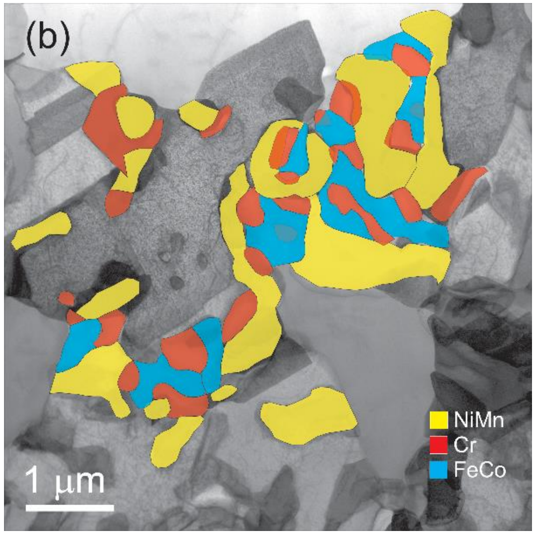
Otto et al, Acta Mater. (2016)

Decomposition into three phases after 500 days at 500 °C

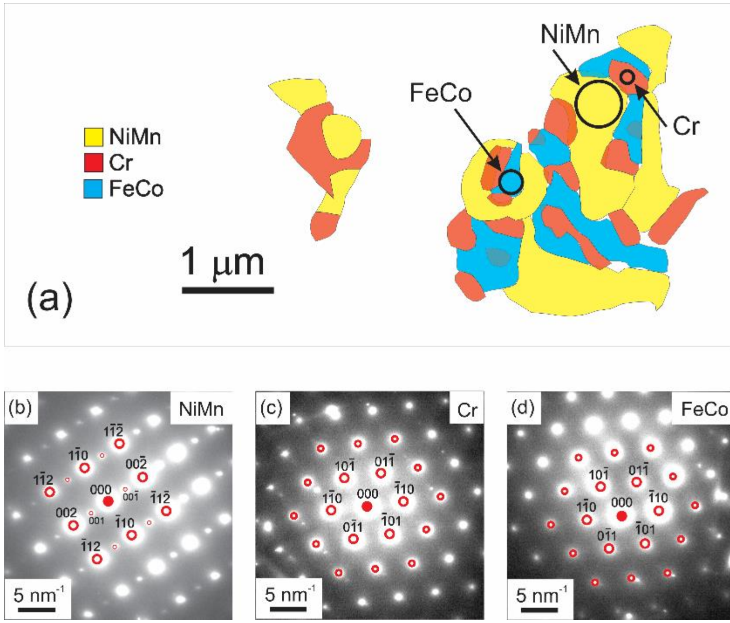
$L1_0$ - NiMn
BCC - Cr
B2 - FeCo



SEM-EDX



TEM-EDX



TEM-SAD

Otto et al, Acta Mater. (2016)

Recommended text books:

(1) R.A. Swalin, Thermodynamics of Solids, 2nd edition, Wiley VCH, New Jersey, 1972

(2) D. R.Gaskell,Introduction to the Thermodynamics of Materials, 5th Edition, CRC Press, New York, 2008

(3) D. Kondepudi, I. Prigogine, Modern Thermodynamics, John Wiley and Sons, Chichester,1998

(4) F.C. Campell, Phase Diagrams – Understanding the Basics, ASM, Ohio, 2012

(5) B. Predel, M. Hoch, M. Pool, Phase Diagrams and Heterogeneous Equilibria, Springer, Berlinm 2004

(6) J.-C. Zhao, Methods for Phase Diagram Determination, Elsevier, Oxford, 2004

(7) D.A. Proter, K.E. Easterling, M. Sherif, Phase Transformations in Metals and Alloys (3rd edition), 2009

More info from teaching assistant ?

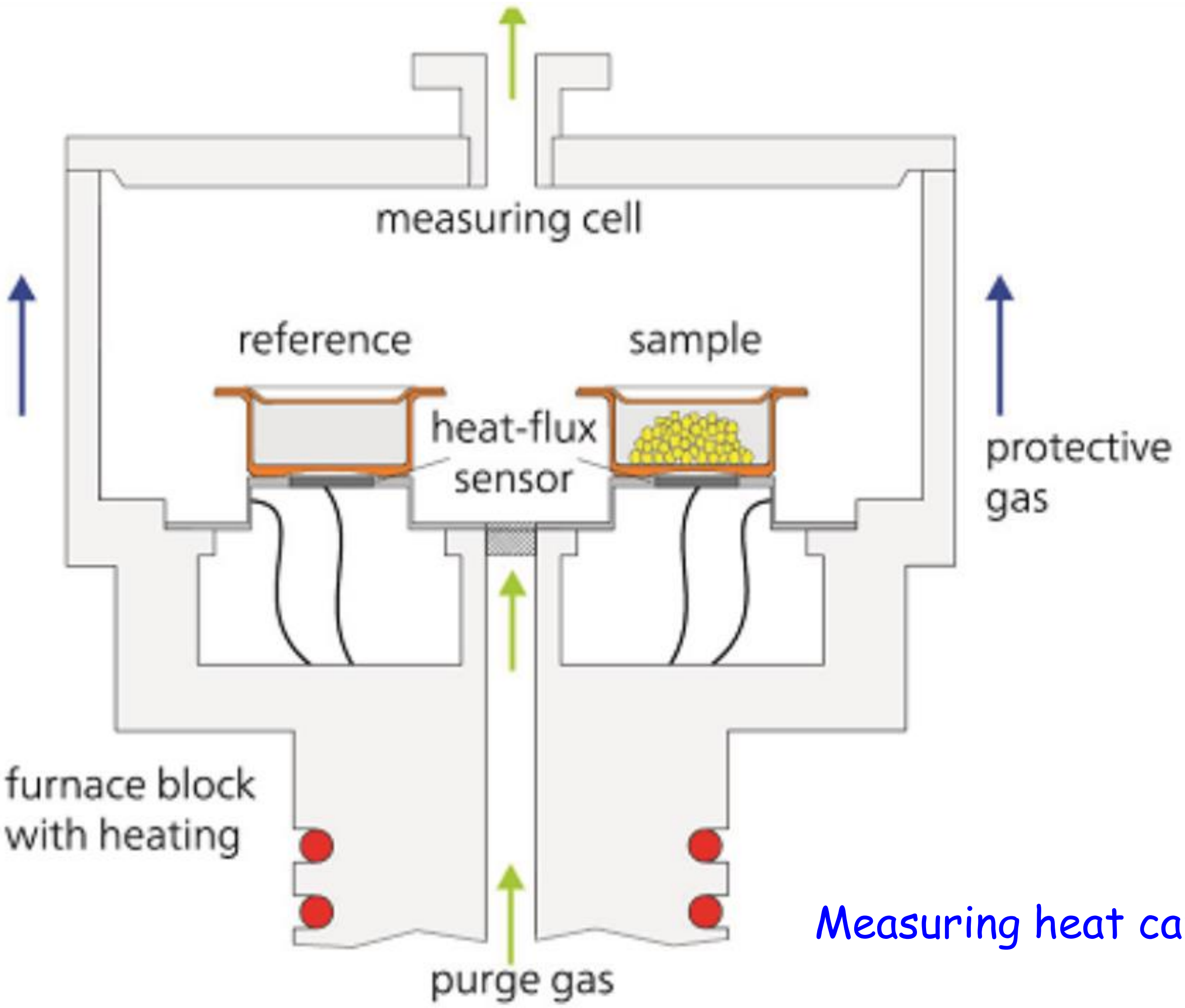
Summary

(1) First law; U, H and c_P
(2) Second law; S and G
(3) Statistical interpretation of S
(4) Driving forces for phase transformations (and heat effects)
(5) Driving forces for mixing
(6) $G(x_i)$-curves and chemical potential μ
(7) Physical justification of phase diagrams
(8) High entropy alloys

Questions for self control

1. What has U and H to do with the first law of thermodynamics?
2. How does the 2nd law help us to derive G?
3. How was the entropy S introduced?
4. What is the statistical interpretation of S?
5. Discuss a simple phase transformation (austenite – martensite) considering G(T)- and H(T)-curves and a related DSC-chart.
6. How does differential scanning calorimetry (DSC) work?
7. What is the chemical potential?
8. Which are the equations for enthalpy and entropy of mixtures?
9. What is the tangent rule and how is it used in G(x)-diagrams?
10. What does equilibrium between two phases mean?
11. Which intermetallic phases do you know?
12. Explain eutectic and peritectic phase diagrams on the basis of underlying G(x)-curves of all relevant phases.
13. What are high entropy alloys?
14. What must elements fulfill to be able to form a high entropy alloy?
15. Why are high entropy alloys an interesting research topic?

Differential scanning calorimeter



Measuring heat capacity (enthalpy)

www. analyzing-testing.netzsch.com/de