



Binary solid mixtures



What happens when we cool down a mixture of chemical elements?

- At high temperatures, in the **gaseous phase**, all **atoms mix**, resulting in a single phase.
- In **liquid phase** they often mix perfectly, but can occasionally also show partial immiscibility (like for example “emulsions” like milk-oil mixtures).
- In **solid phase** often phase separation between solution of element B in element A (α -phase) and solution of element A in element B (β -phase) exists – **a binary alloy**.
- The phase transition from liquid to solid phase in such mixtures shows a characteristic phase diagram, in which **three components react with each other** (e.g. liquid, α -phase, β -phase).
- These reactions are classified into **eutectic, peritectic and monotectic**.

Phase diagrams of two-component (“binary”) alloy systems:

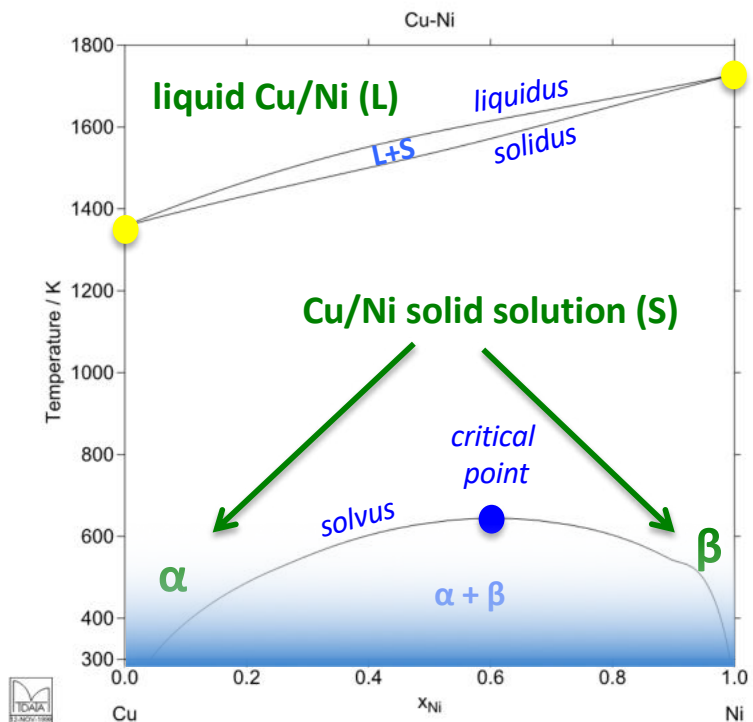
often characterized by limited solubility of each of the components in the other

Solubility phase diagrams:

example: Copper-Nickel alloy

solid phases (below critical point):
Cu-rich (α)

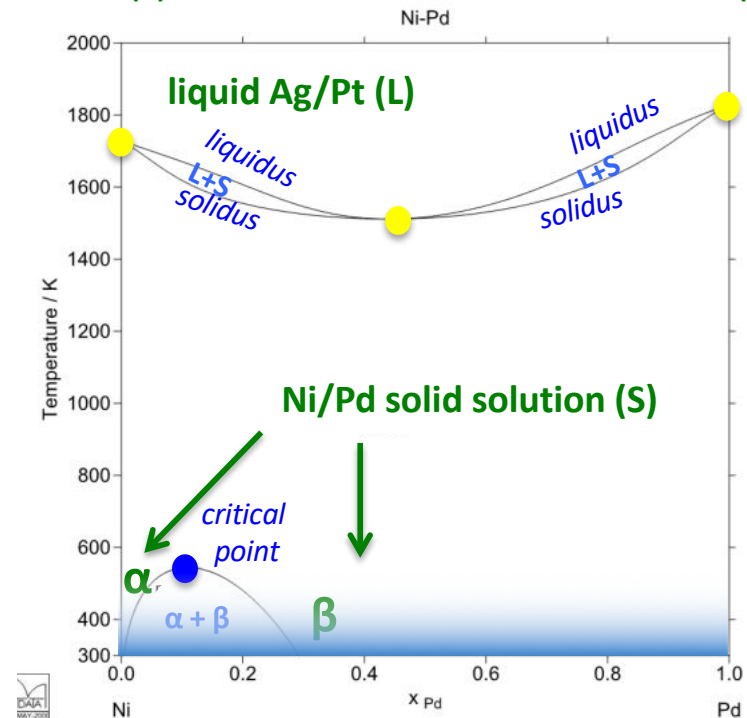
Ni-rich (β)



example: Nickel-Palladium alloy

solid phases (below critical point):
Ni-rich (α)

Pd-rich (β)



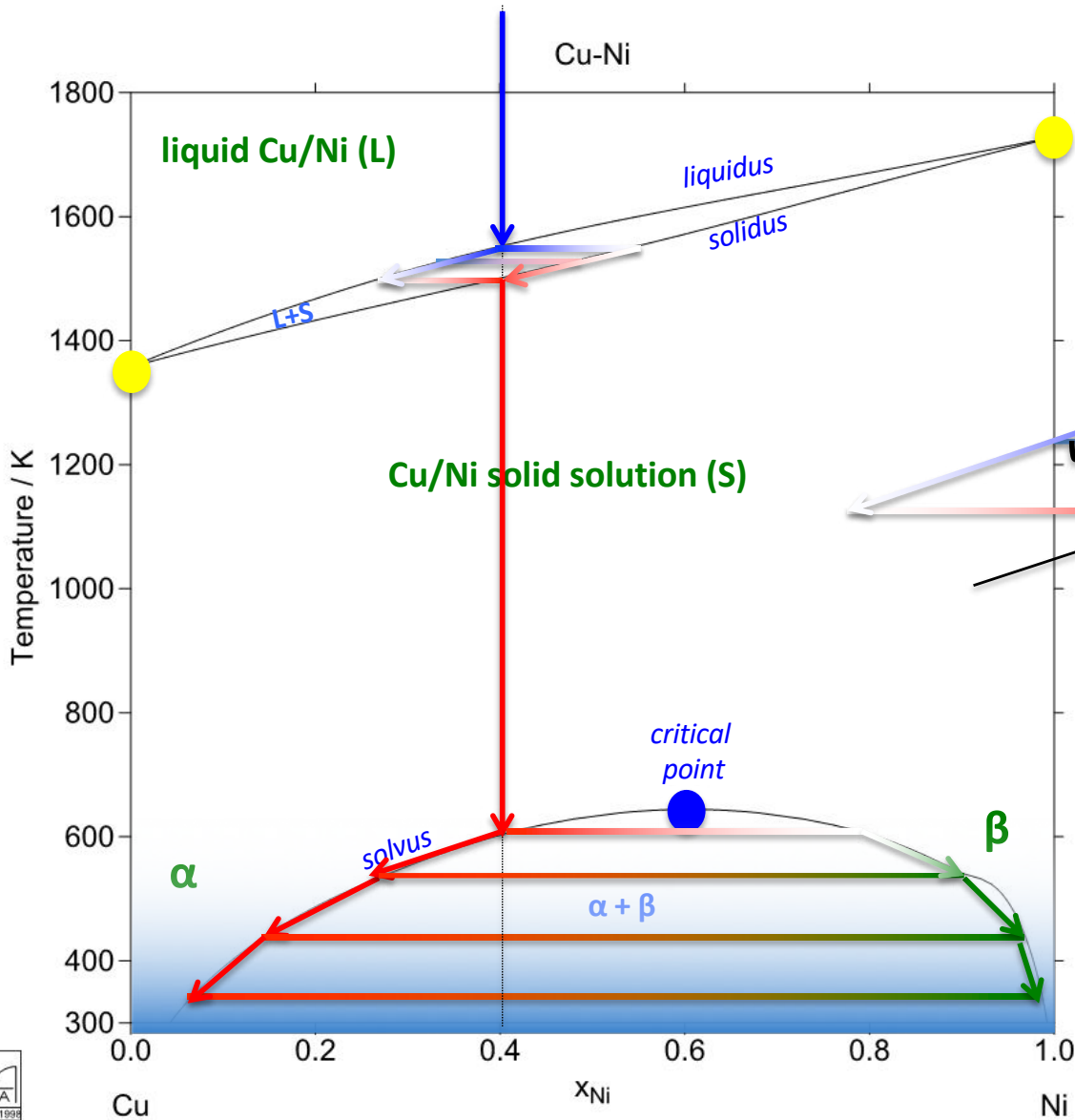
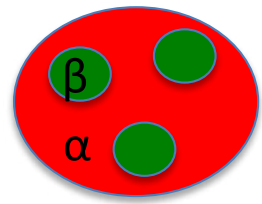
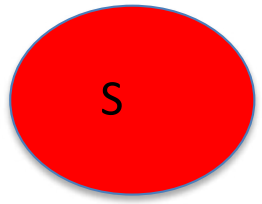
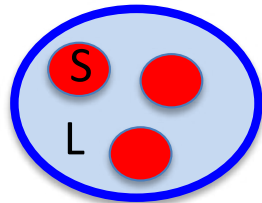
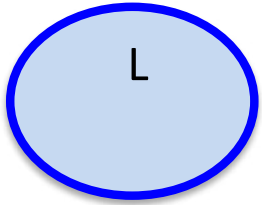
Data source: National Physical Laboratory (NPL) online service:

<http://resource.npl.co.uk/mtdata/phdiagrams/png/cuni.png>

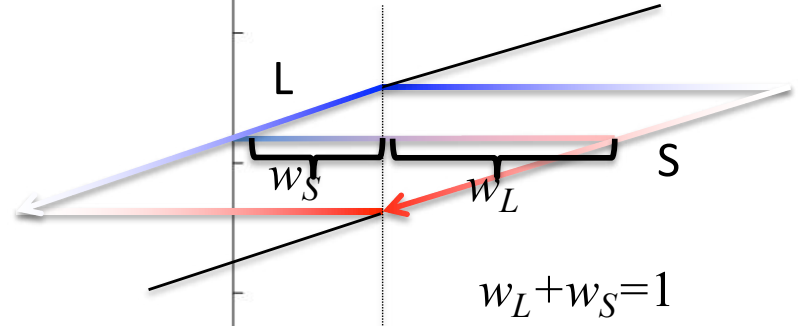
<http://resource.npl.co.uk/mtdata/phdiagrams/png/nipd.png>



solid phases (below critical point):
Cu-rich (α) Ni-rich (β)



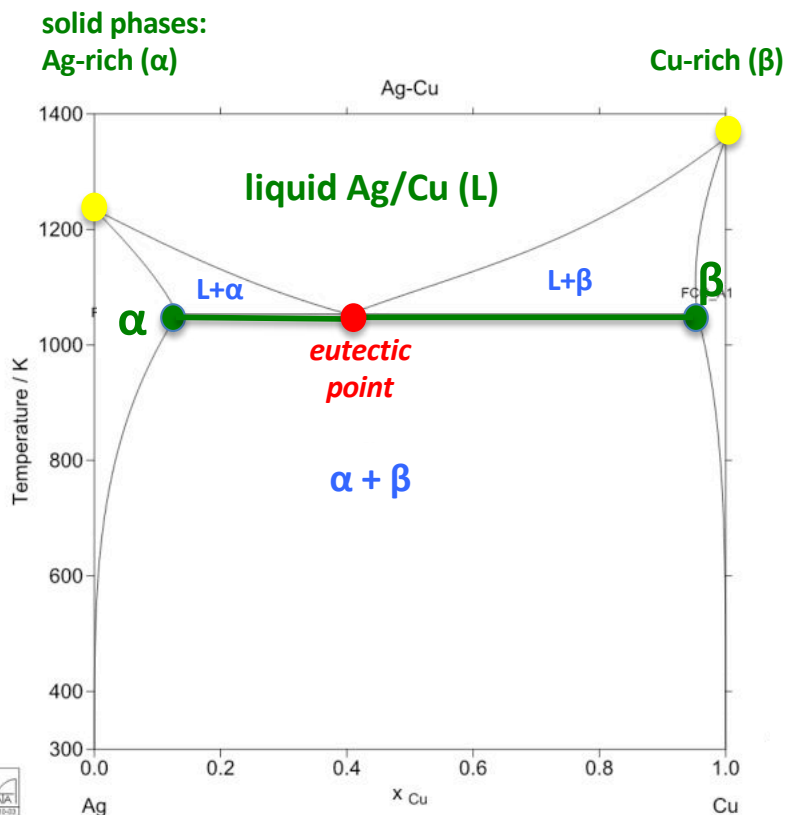
lever rule for relative fraction of phases



Phase diagrams of two-component (“binary”) alloy systems:

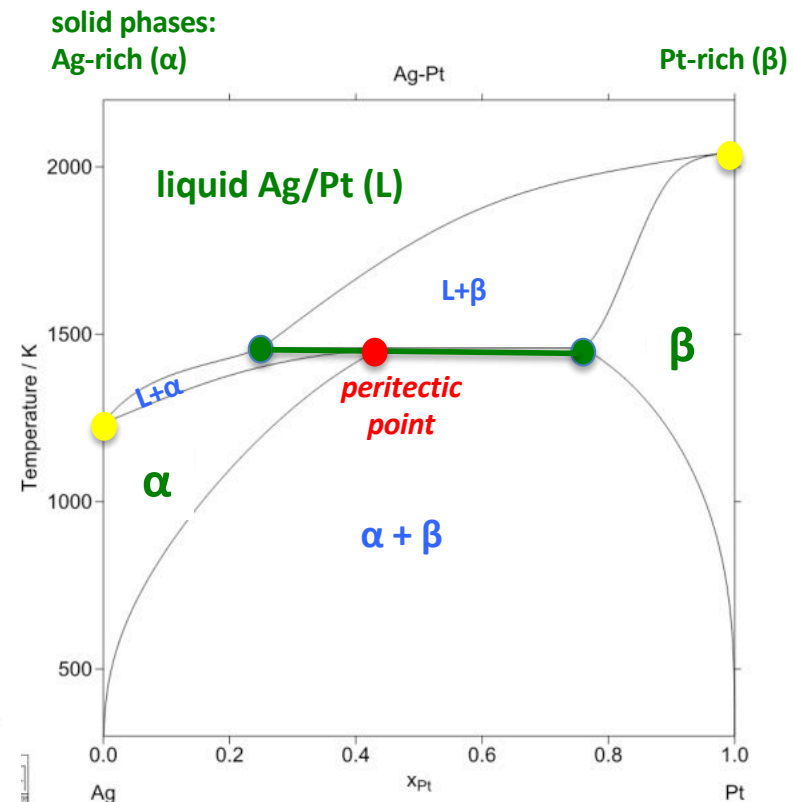
often characterized by limited solubility of each of the components in the other

Eutectic phase diagram example: Silver-Copper alloy

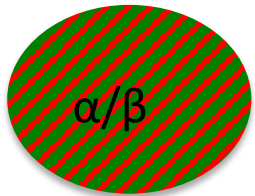
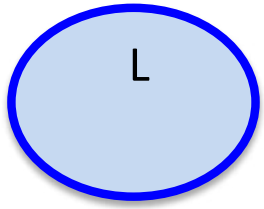


eutectic transition: $L \rightarrow \alpha + \beta$

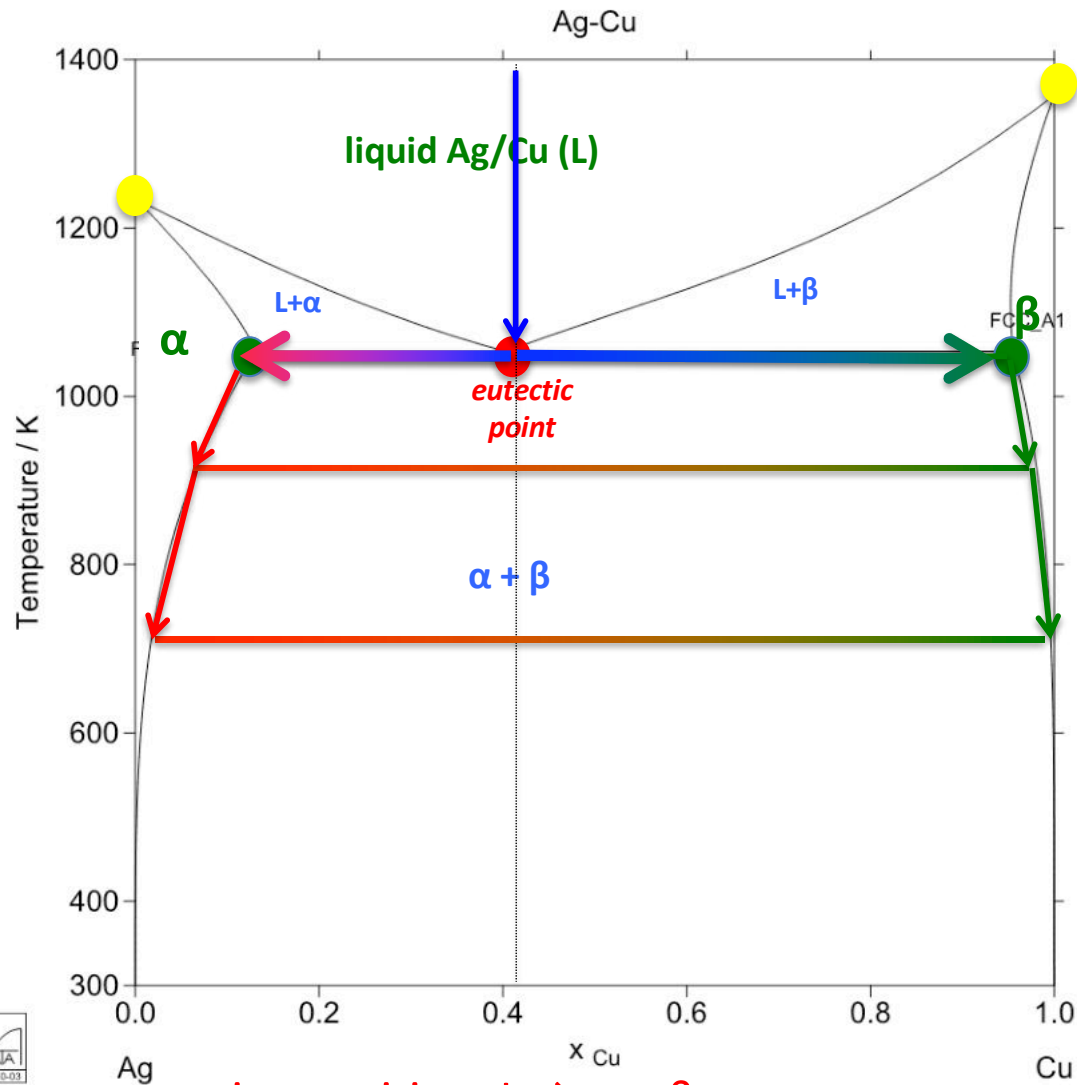
Peritectic phase diagram example: Silver-Platinum alloy



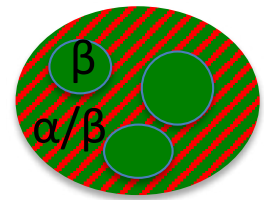
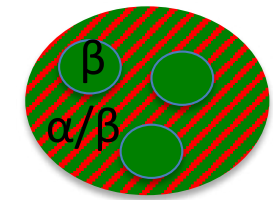
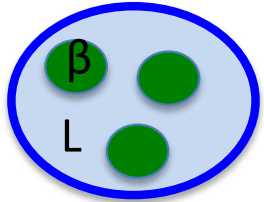
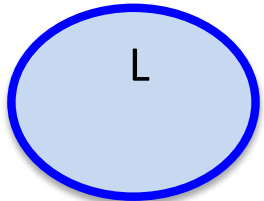
peritectic transition $L + \beta \rightarrow \alpha$



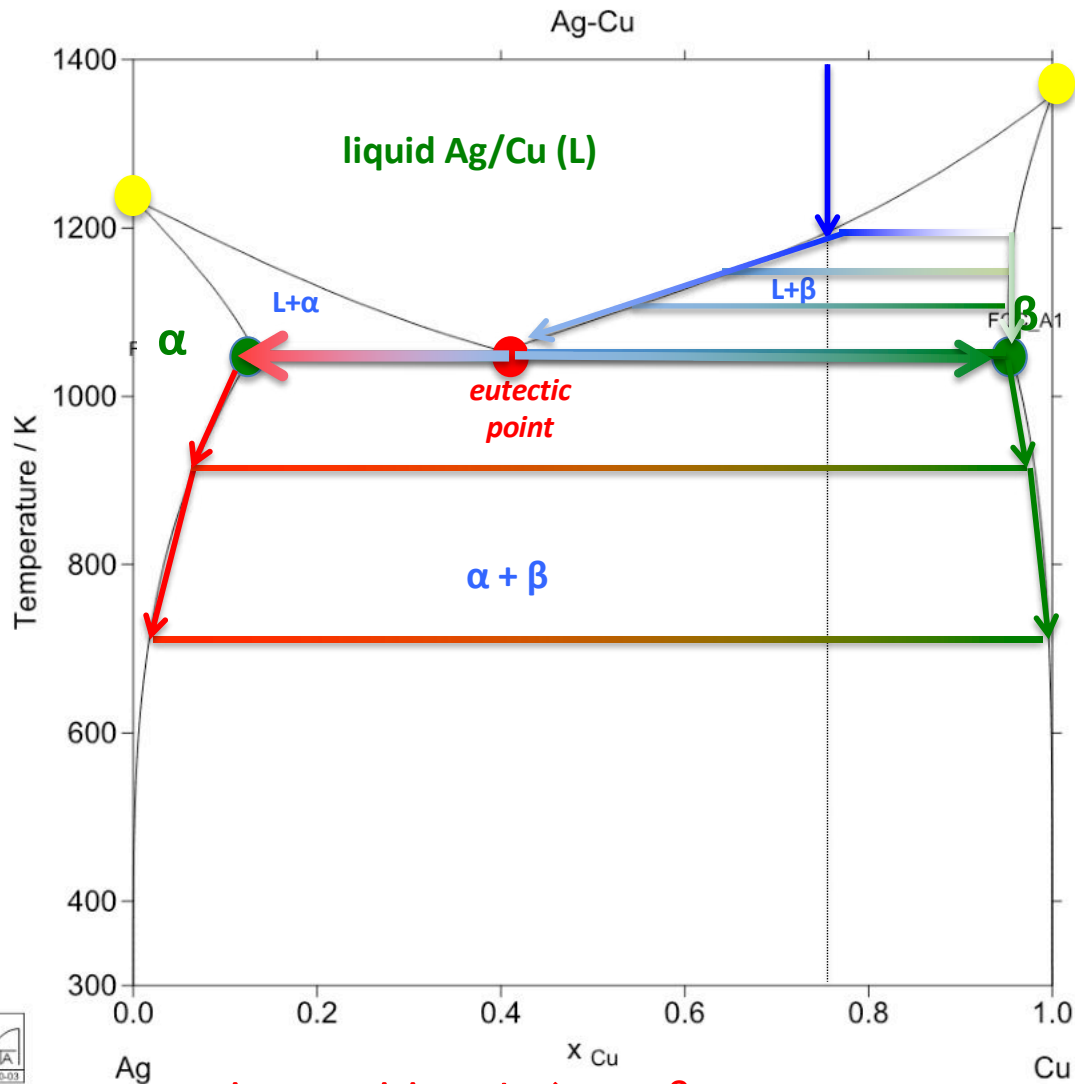
solid phases:
Ag-rich (α)
Cu-rich (β)



eutectic transition: $L \rightarrow \alpha + \beta$



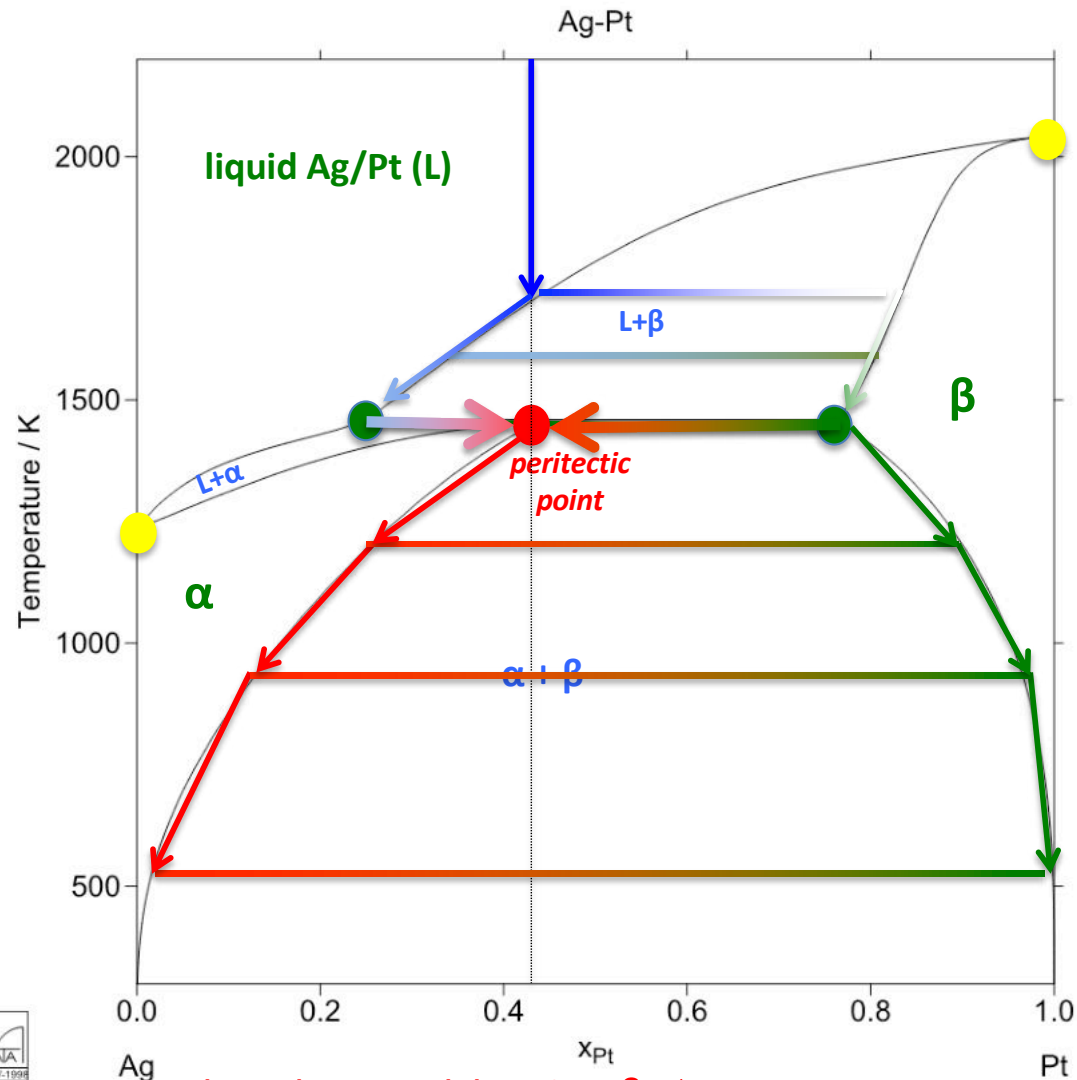
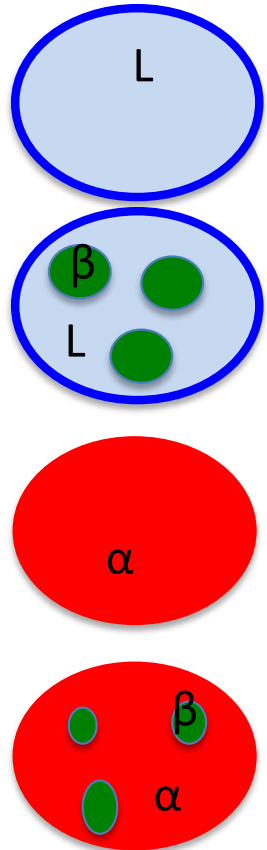
solid phases:
Ag-rich (α)
Cu-rich (β)



eutectic transition: $L \rightarrow \alpha + \beta$

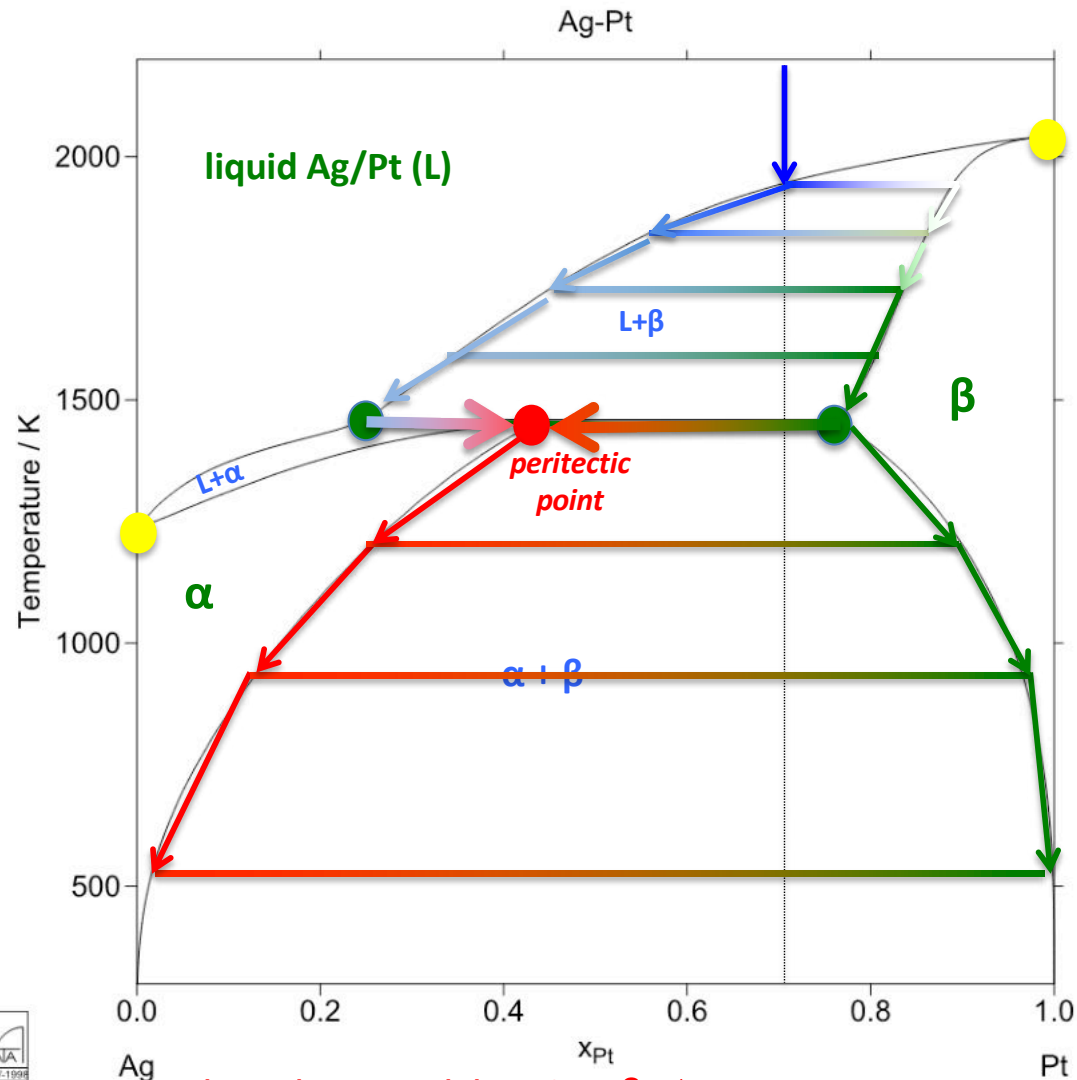
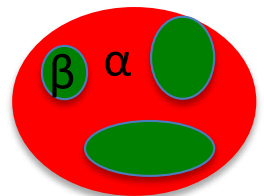
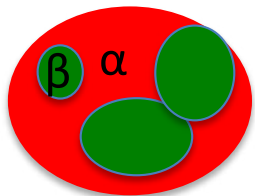
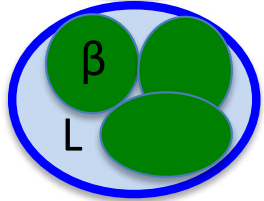
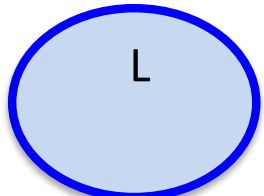
solid phases:
Ag-rich (α)

Pt-rich (β)



solid phases:
 Ag-rich (α)

Pt-rich (β)



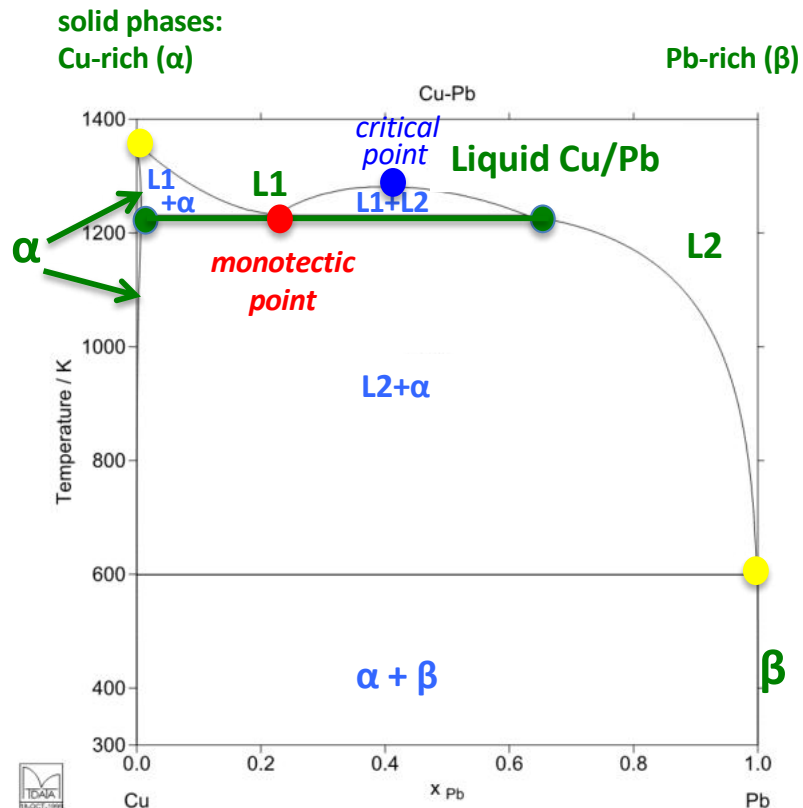
peritectic transition $L + \beta \rightarrow \alpha$



Phase diagrams of two-component (“binary”) alloy systems:

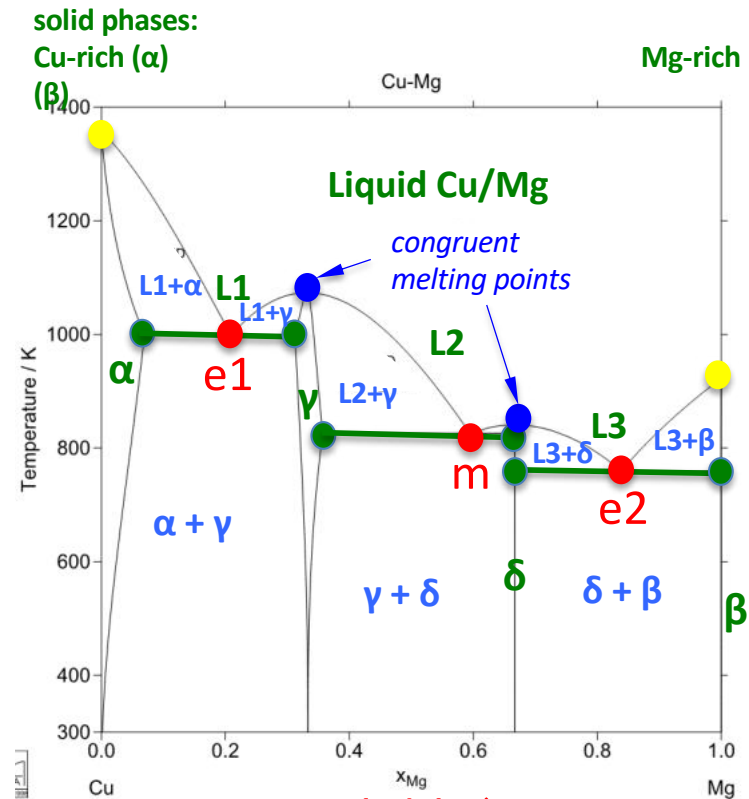
often characterized by limited solubility of each of the components in the other

Monotectic phase diagram example: Copper-Lead alloy



monotectic transition: $L1 \rightarrow \alpha + L2$

More complex phase diagrams example: Copper-Magnesium alloy

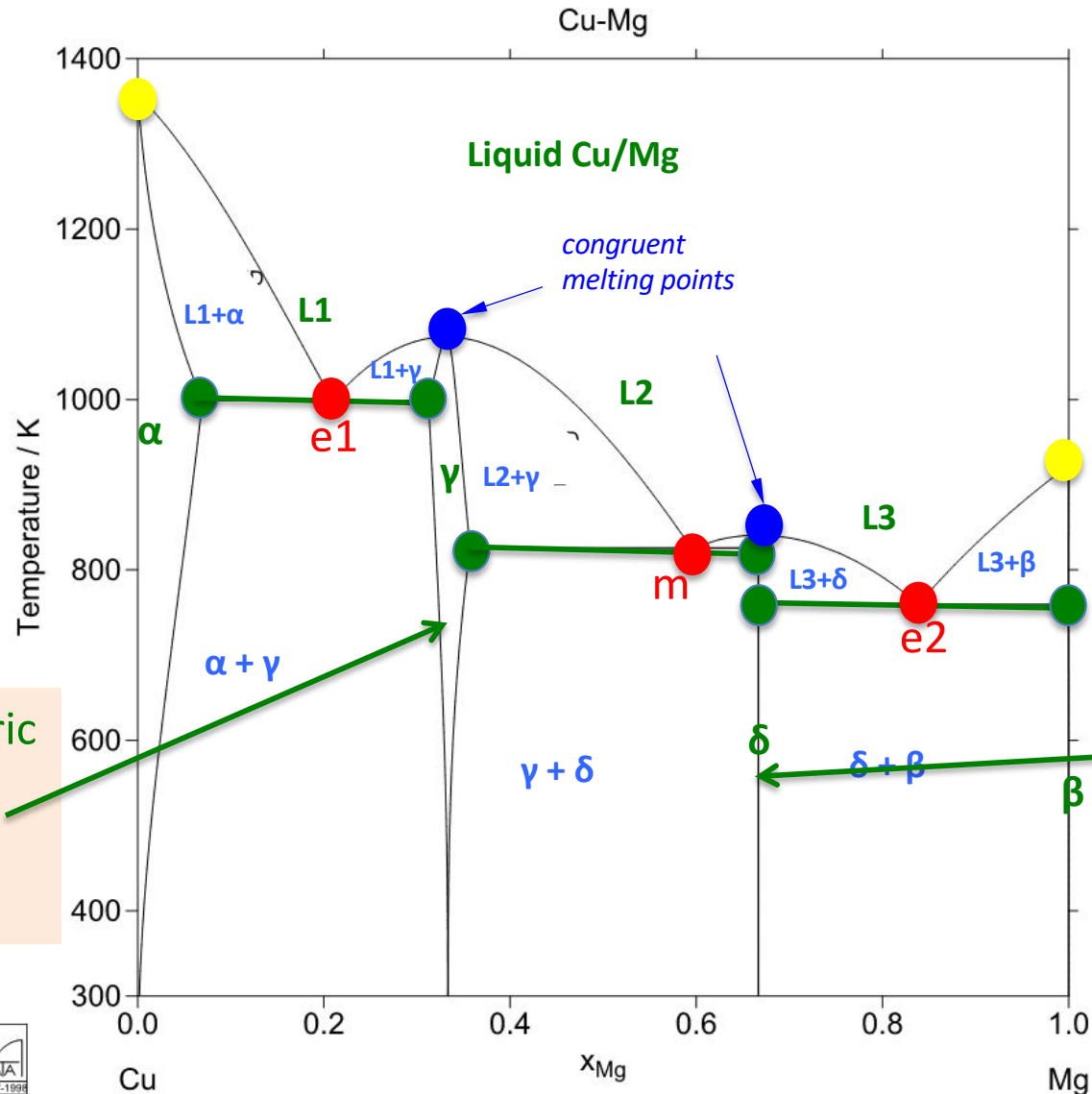


e1: $L1 \rightarrow \alpha + \gamma$,
m: $L2 \rightarrow \gamma + L3$,
e2: $L3 \rightarrow \delta + \beta$

Data source: National Physical Laboratory (NPL) online service:
<http://resource.npl.co.uk/mtdata/phdiagrams/png/agpb.png>
<http://resource.npl.co.uk/mtdata/phdiagrams/png/cumg.png>

solid phases:
Cu-rich (α)

Mg-rich (β)



Non-stoichiometric compound
Laves C15 phase
($MgCu_2$)

Stoichiometric (intermetallic) compound
 $CuMg_2$



Thermodynamics background: Consider two chemical components, A and B (e.g. A=Ag, B=Cu).

1.) Gibbs free enthalpy of a real binary mixture at constant pressure:

For each phase of a binary mixture the Gibbs free energy is given as: (Note that $x_A=1-x_B$)

$$G(T, x_B)/N = x_A \mu_{A,0}(T) + x_B \mu_{B,0}(T) + k_B T (x_A \ln x_A + x_B \ln x_B) + x_A x_B [a(T) + (x_A - x_B) b(T)]$$

Interpolates linearly
Between pure
compound Gibbs FE's

Contribution due to
"mixing entropy"; this
term is always negative.

"Excess enthalpy"; quantifies
deviation from ideal behavior.
Can be positive or negative.
 a and b are functions of T

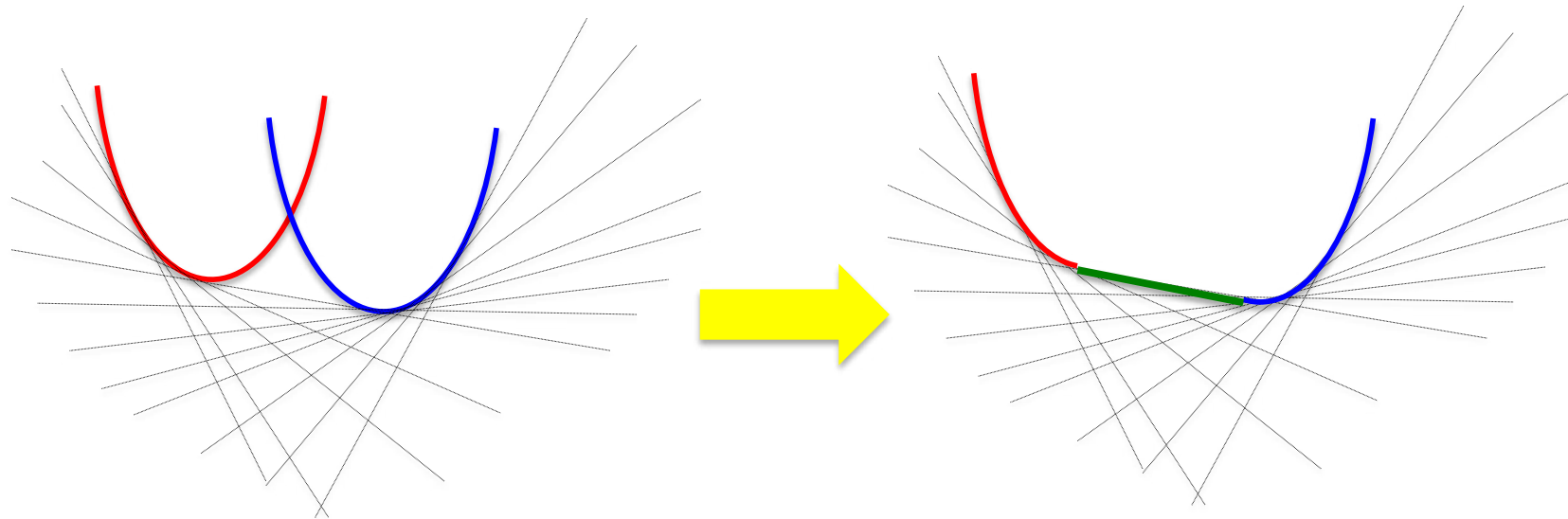
The first term is a linear function of x_B that interpolates between the Gibbs free enthalpies of the pure compounds.

The second term is due to the mixing of atoms A and B. It is zero in the pure compounds and negative in between.

The excess enthalpy is due to the fact that the average energy for interactions between A and B atoms is not the same as that for A-A and B-B interactions.

In so-called ideal mixtures it is negligible (this defines ideal mixtures). This term also is zero in the pure compounds. If the attractive interactions between A-B are on average weaker than that for A-A and B-B, this term is positive.

The construction of the lower convex hull to two curves:



Find the set of all tangents to the two curves that fulfill the condition to lie entirely below both curves. Then find the envelope for these tangents (the “caustic”). The picture above illustrates the procedure.

In our case it is the correct construction to find the **equilibrium state between two phases** from the two Gibbs free energy curves of each phase. The red and blue curves will e.g. correspond to the liquid and solid phases, and the green line to the coexistence region. It is defined as a tangent to both the red and blue curves. The envelope curve (red+green+blue) defines the thermodynamic stable state.

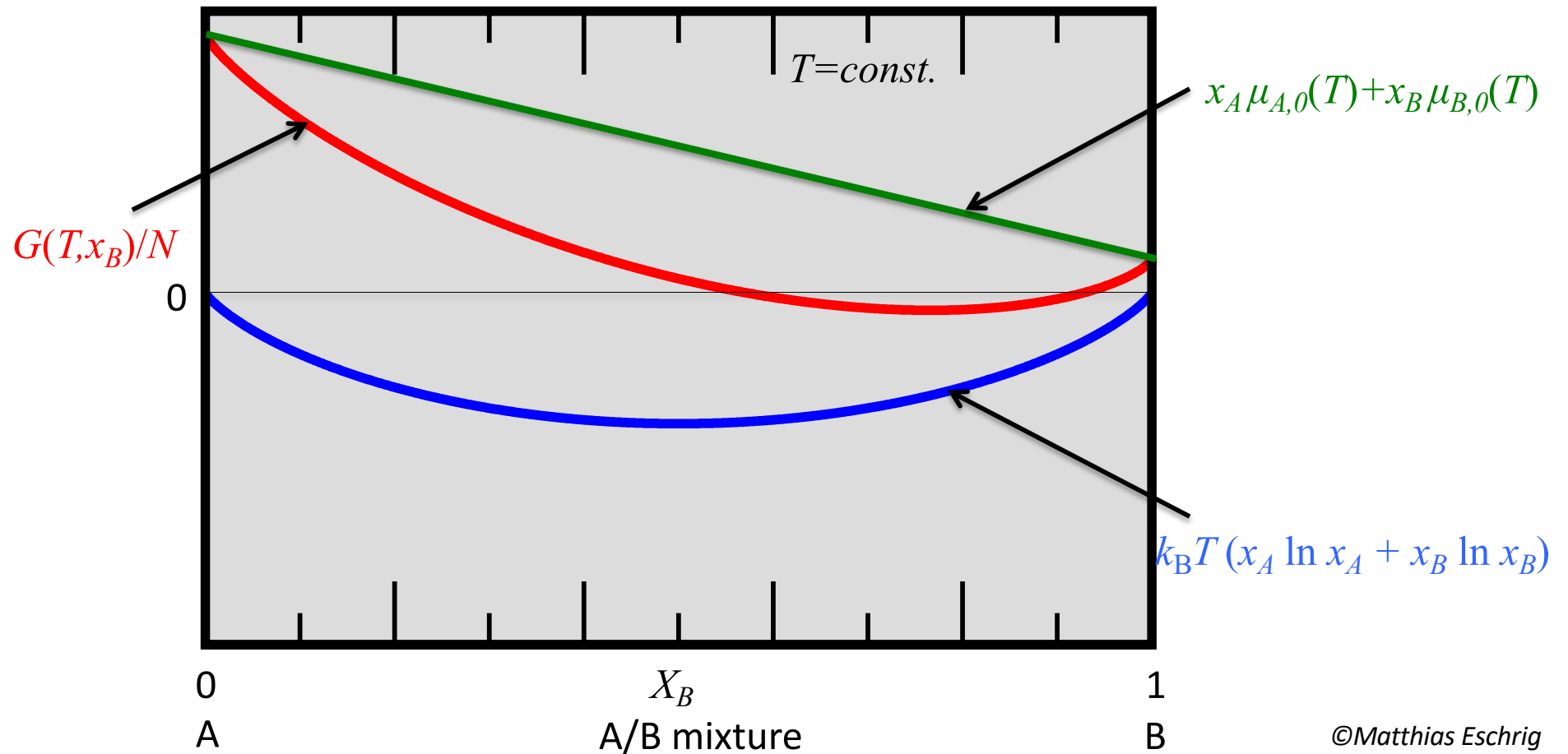


Gibbs free energy for ideal mixture:

Ideal mixtures are mixtures where the excess enthalpy term can be neglected:

$$G(T, x_B)/N = x_A \mu_{A,0}(T) + x_B \mu_{B,0}(T) + k_B T (x_A \ln x_A + x_B \ln x_B)$$

Let us fix T and study the qualitative dependence on x_B :



Gibbs free energy for ideal mixture:

Ideal mixtures are mixtures where the excess enthalpy term can be neglected:

$$G(T, x_B)/N = \underbrace{x_A \mu_{A,0}(T) + x_B \mu_{B,0}(T)}_{\text{linear term}} + \underbrace{k_B T (x_A \ln x_A + x_B \ln x_B)}_{\text{mixing entropy}}$$

There is a version for the liquid state, $G^L(T, x_B)/N^L$, and a version for the solid state, $G^S(T, x_B)/N^S$. Each of these versions of this equation has its own set of parameters.

When lowering temperature, the chemical potentials $\mu_{A,0}^S(T)$ and $\mu_{B,0}^S(T)$ for the solid increase less rapidly than $\mu_{A,0}^L(T)$ and $\mu_{B,0}^L(T)$ for the liquid, as the pure solid phases must have a lower Gibbs free energy at low temperatures than the pure liquid phases.

The mixing entropy term decreases in magnitude with decreasing temperature (it is $\sim T$).

In the following pictures we take a model material with the following parameters (all parameters are related to 1 mol, i.e. to Avogadro's number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$):

$$N_A [\mu_{A,0}^S(T) - \mu_{A,0}^L(T)] = (-59725 + 48.35 T) \text{ J/mol}$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$N_A [\mu_{B,0}^S(T) - \mu_{B,0}^L(T)] = (-75270 + 48.10 T) \text{ J/mol}$$

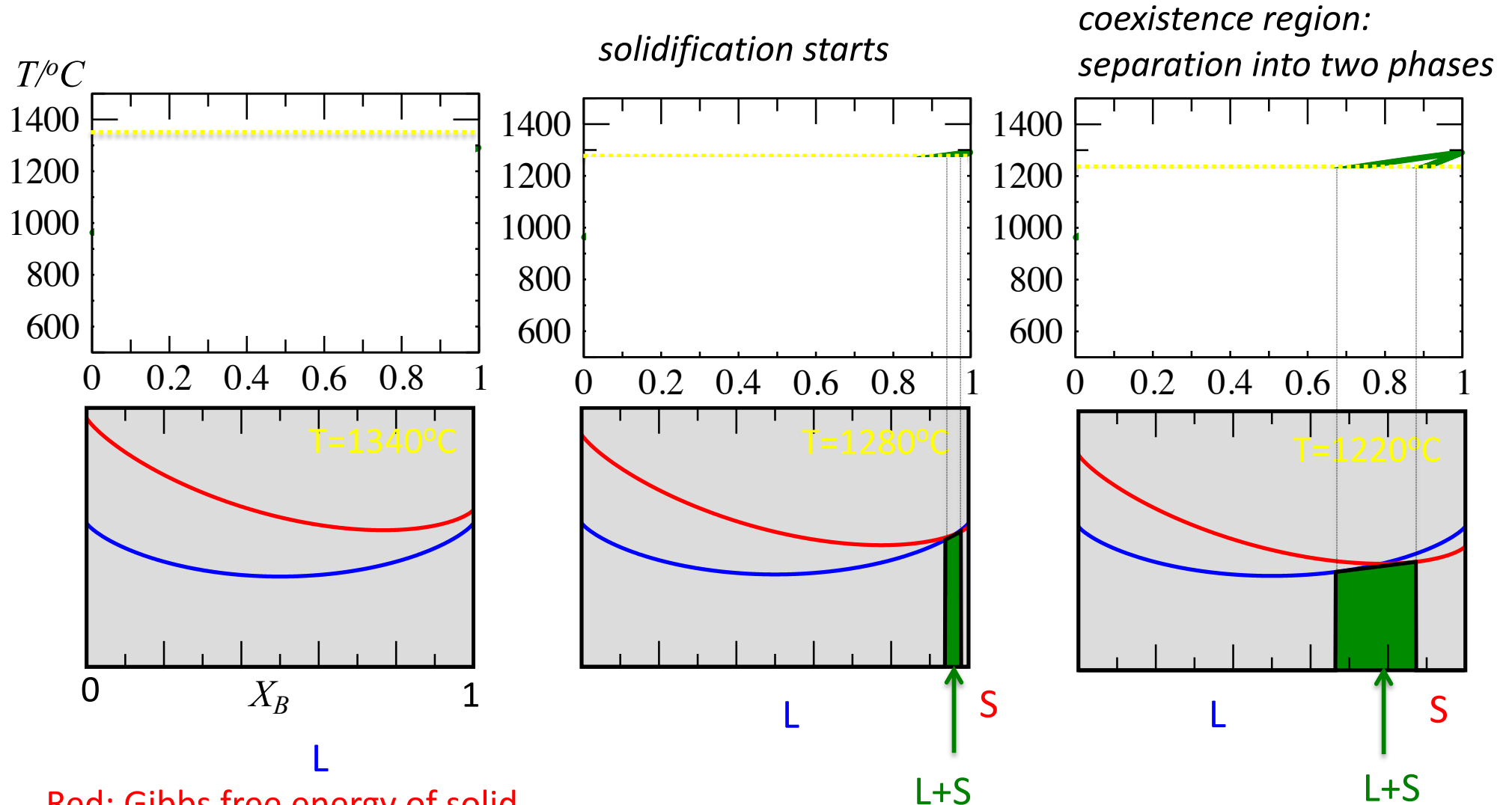
$$N_A k_B = R = 8.314 \text{ J/(mol K)}$$

$$\mu_{A,0}^L(T) = \mu_{B,0}^L(T)$$



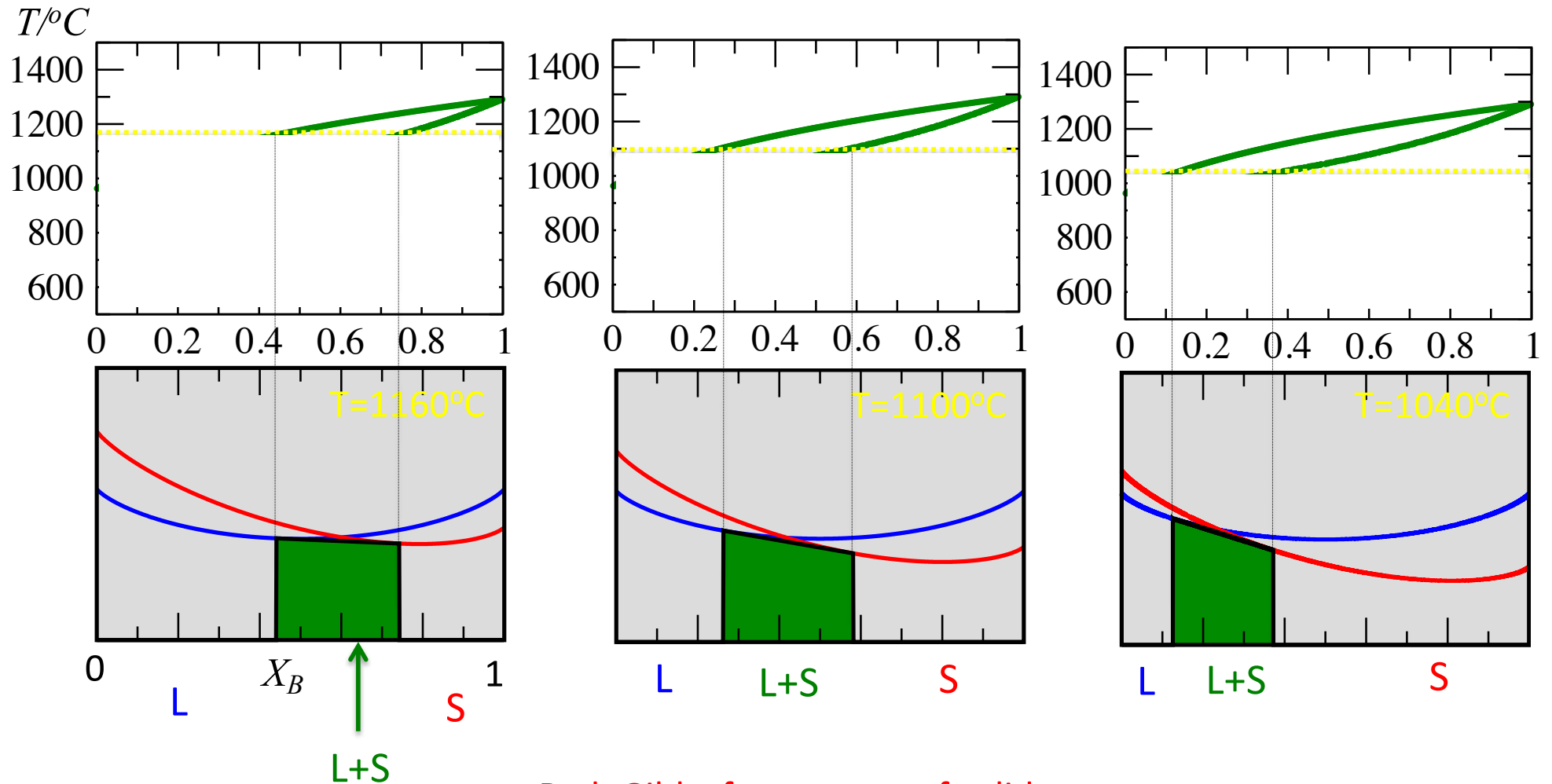
Gibbs free energy for ideal mixture:

In the following series of graphs (next three slides) the temperature (yellow line) is gradually lowered:



Red: Gibbs free energy of solid
 Blue: Gibbs free energy of liquid

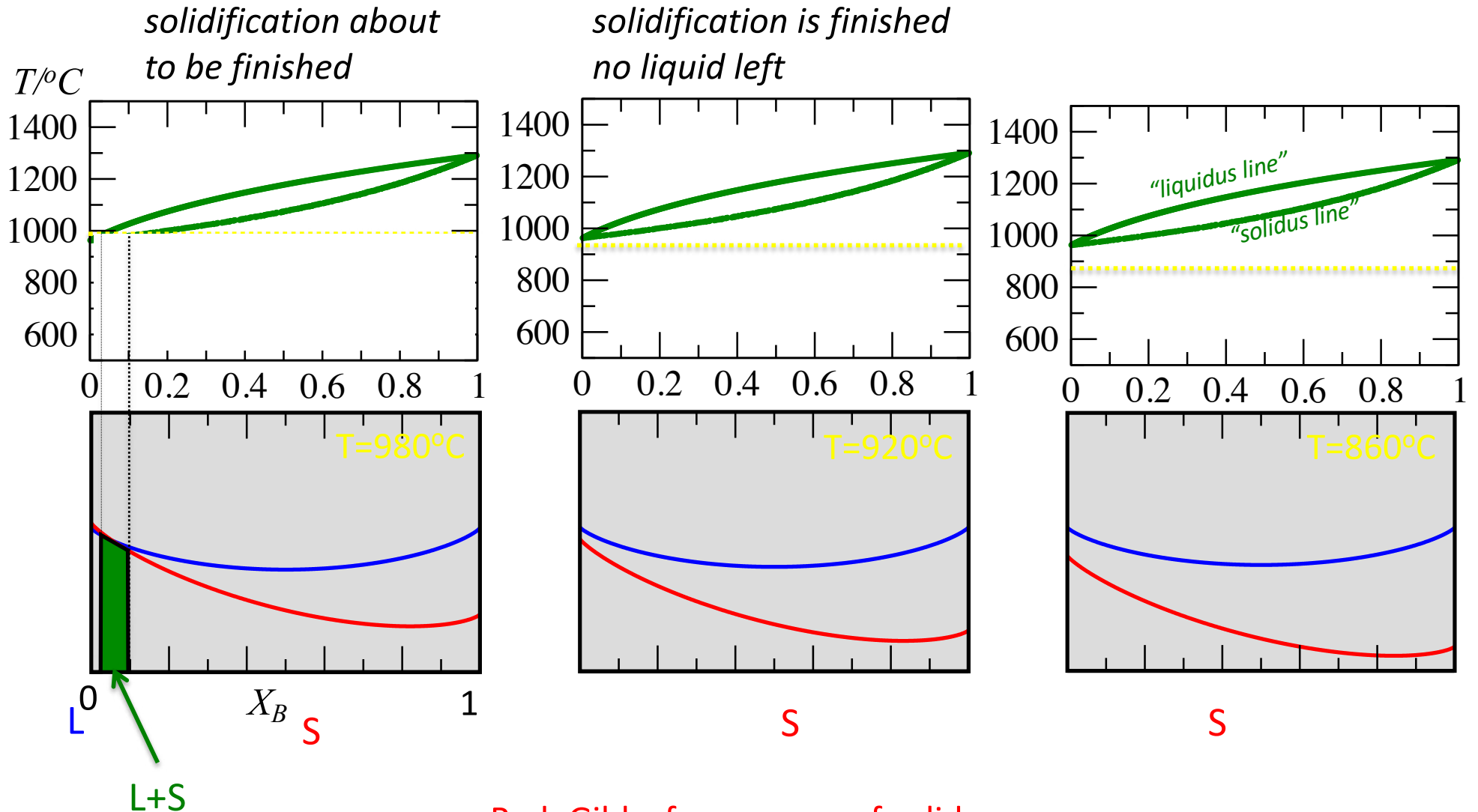
Gibbs free energy for ideal mixture:



Red: Gibbs free energy of solid
Blue: Gibbs free energy of liquid



Gibbs free energy for ideal mixture:

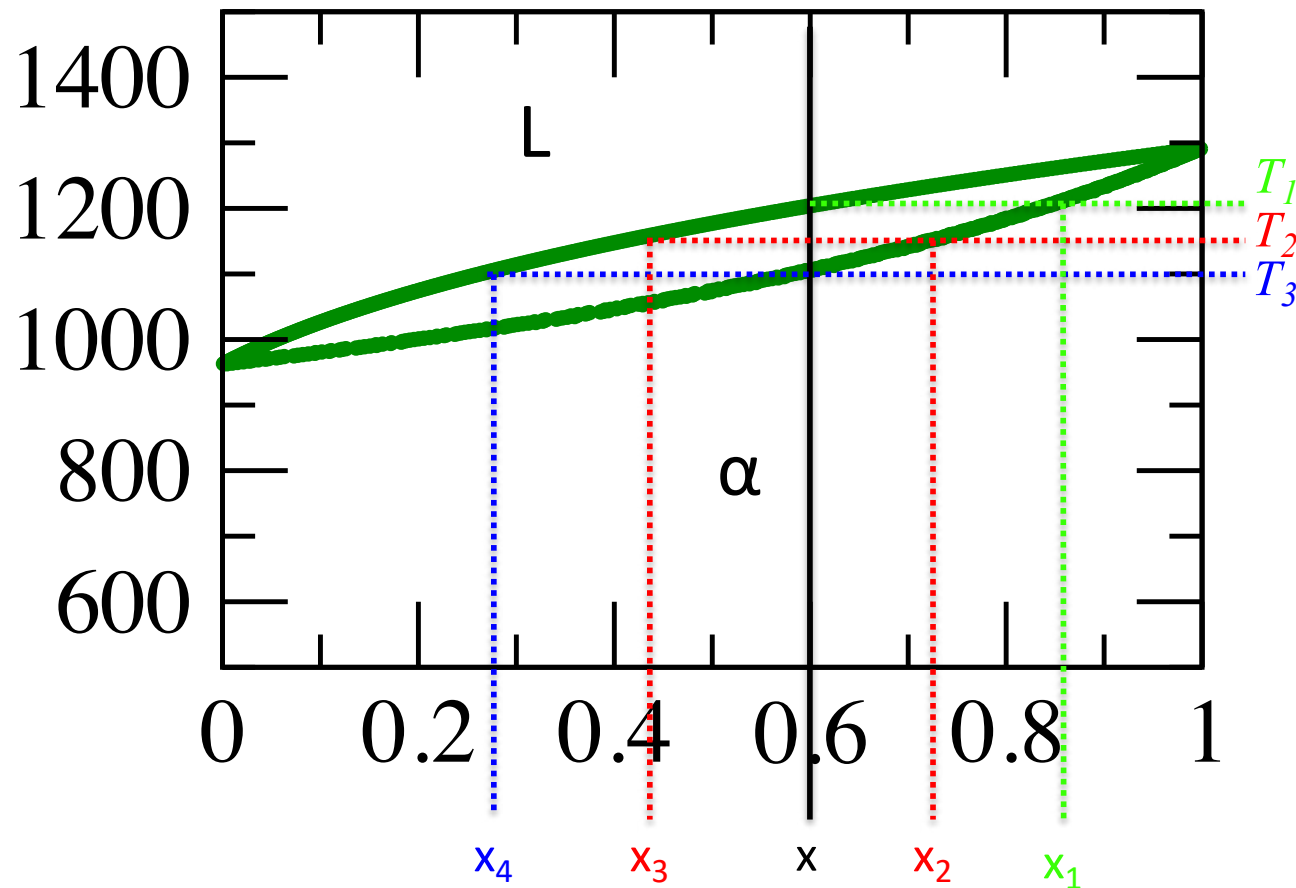


Red: Gibbs free energy of solid
 Blue: Gibbs free energy of liquid



2.) Composition and substance fraction of phases:

A) What is the composition of the phases?



	L	α
T_1	x	x_1
T_2	x_3	x_2
T_3	x_4	x

above T_1 there is only liquid with composition x

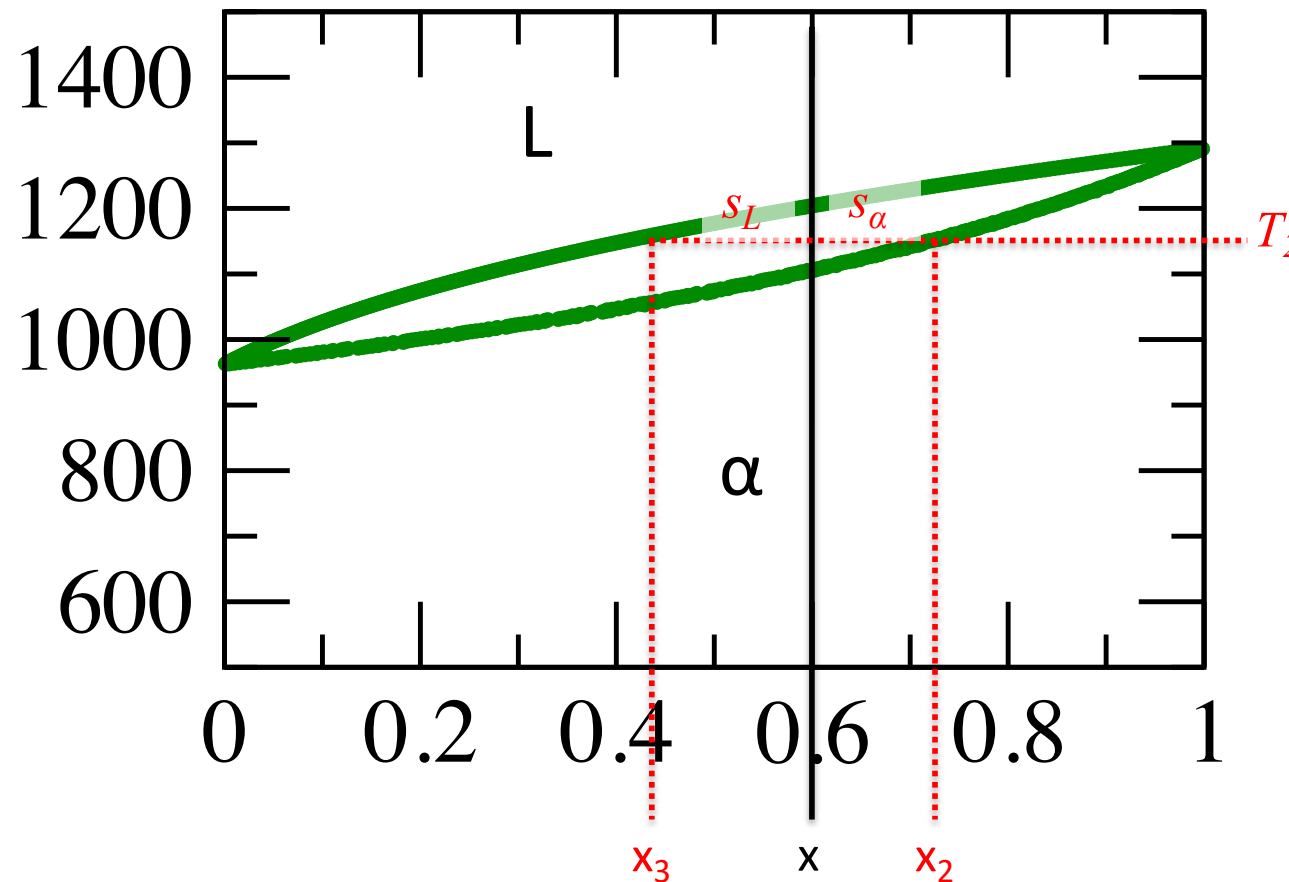
below T_3 there is only solid with composition x

Between T_1 and T_3 the composition of the liquid changes from x to x_4 and the composition of the solid changes from x_1 to x.



2.) Composition and substance fraction of phases:

B) What is the fraction of each of the two phases?



“Lever rule”:

$$w_\alpha + w_L = 1$$

$$w_\alpha S_\alpha + w_L S_L = S_\alpha + S_L$$



$$w_\alpha = S_L / (S_\alpha + S_L) = (x - x_3) / (x_2 - x_3)$$

$$w_L = S_\alpha / (S_\alpha + S_L) = (x_2 - x) / (x_2 - x_3)$$

3.) Gibbs free energy leading to a miscibility gap:

In real mixtures the excess term becomes important:

$$G(T, x_B)/N = \underbrace{x_A \mu_{A,0}(T) + x_B \mu_{B,0}(T)}_{\text{linear term}} + \underbrace{k_B T (x_A \ln x_A + x_B \ln x_B)}_{\text{mixing entropy}} + \underbrace{x_A x_B [a(T) + (x_A - x_B) b(T)]}_{\text{excess enthalpy}}$$

Again, there is a version of this equation for the liquid phase, $G^L(T, x_B)/N^L$, and a version for the solid phase, $G^S(T, x_B)/N^S$. Each of these versions has its own set of parameters.

In the following pictures we take a model material with the following parameter set:

$$N_A [\mu_{A,0}^S(T) - \mu_{A,0}^L(T)] = (-59725 + 48.35 T) \text{ J/mol}$$

$$N_A [\mu_{B,0}^S(T) - \mu_{B,0}^L(T)] = (-75270 + 48.10 T) \text{ J/mol}$$

$$\mu_{A,0}^L(T) = \mu_{B,0}^L(T)$$

$$N_A k_B = R = 8.314 \text{ J/(mol K)}$$

$$a^S(T) = (20719.2 - 5.5068 T) \text{ J/mol}$$

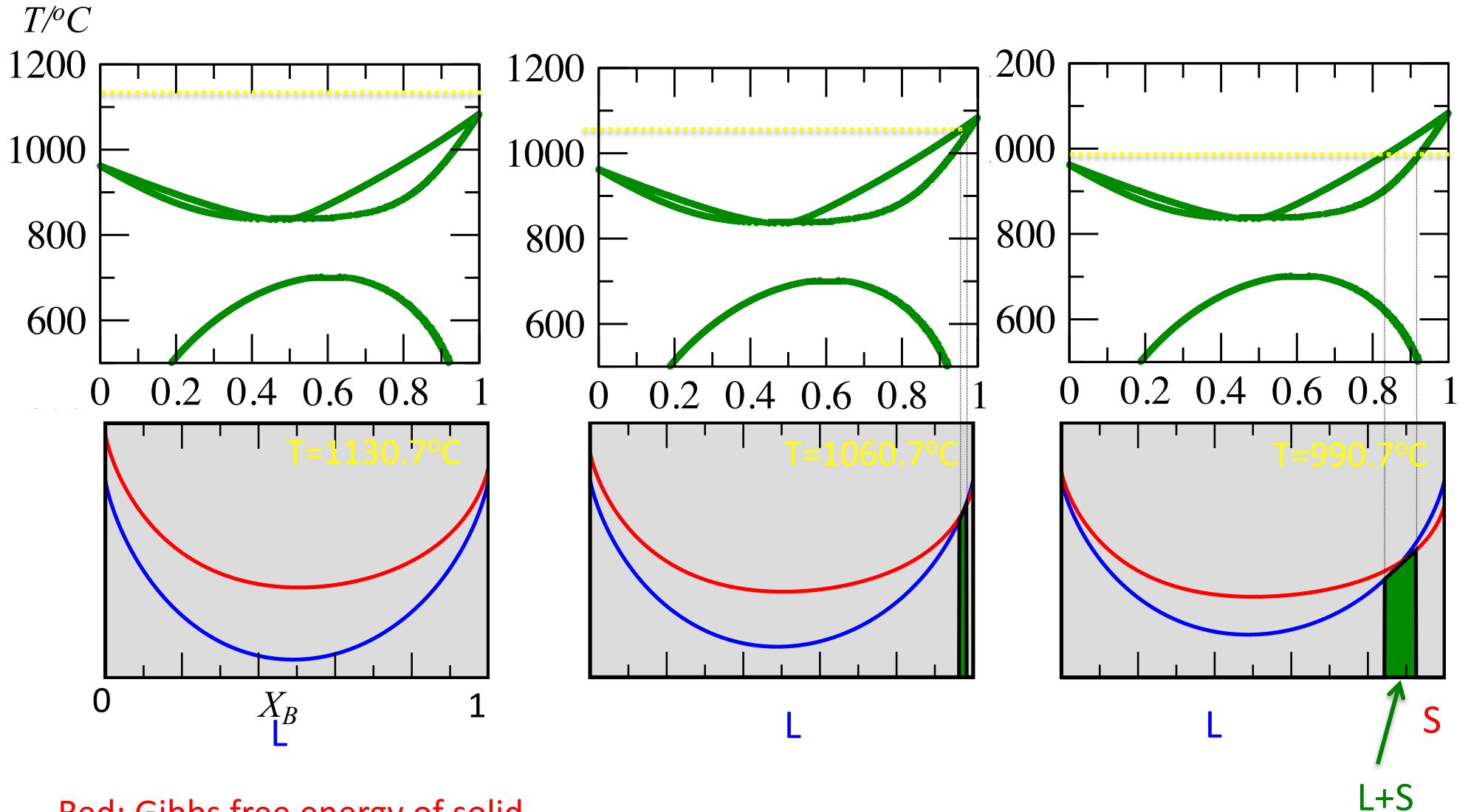
$$b^S(T) = (-3597.6 + 1.035 T) \text{ J/mol}$$

$$a^L(T) = (9102.6 - 1.5222 T) \text{ J/mol}$$

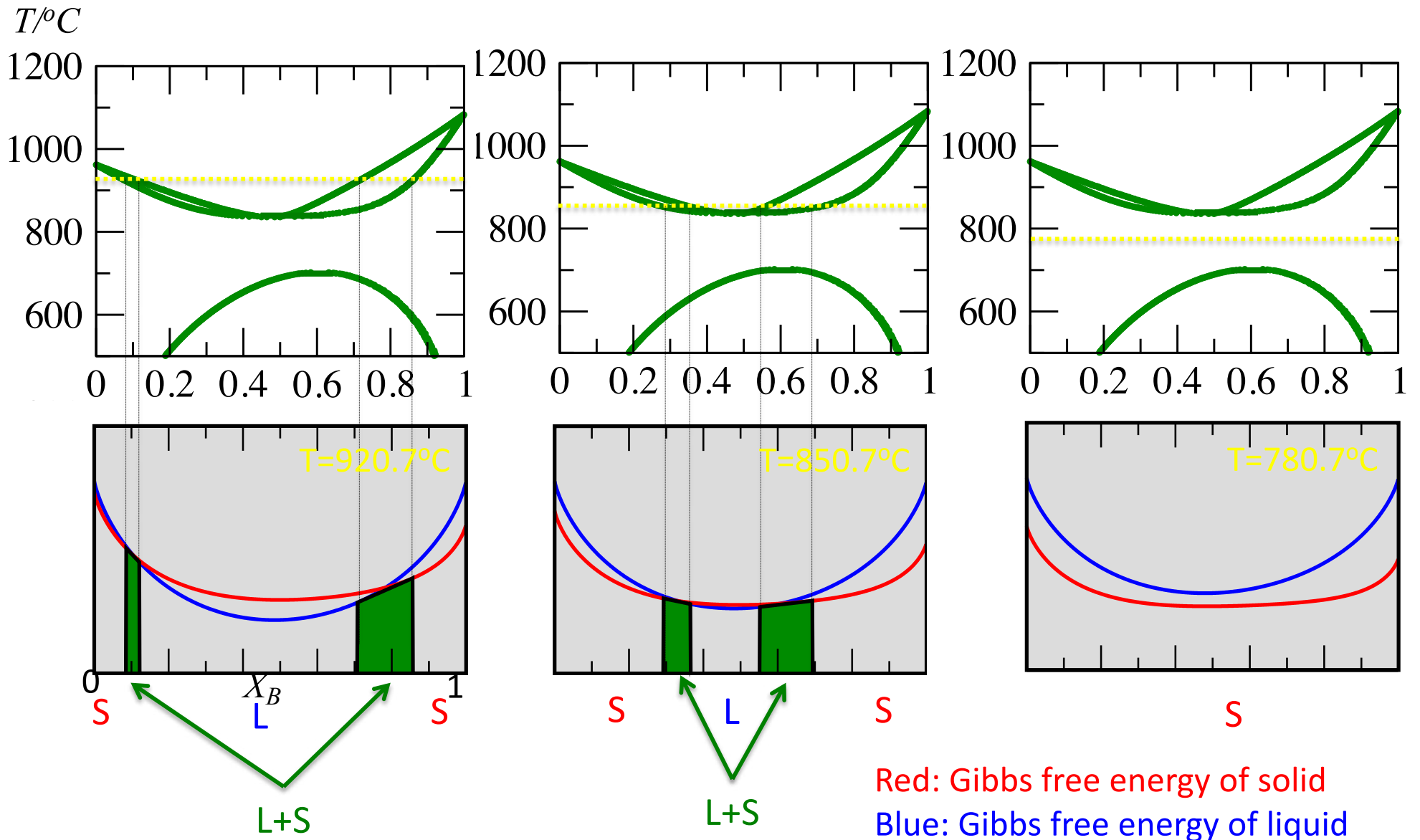
$$b^L(T) = (-1455 + 0.5676 T) \text{ J/mol}$$

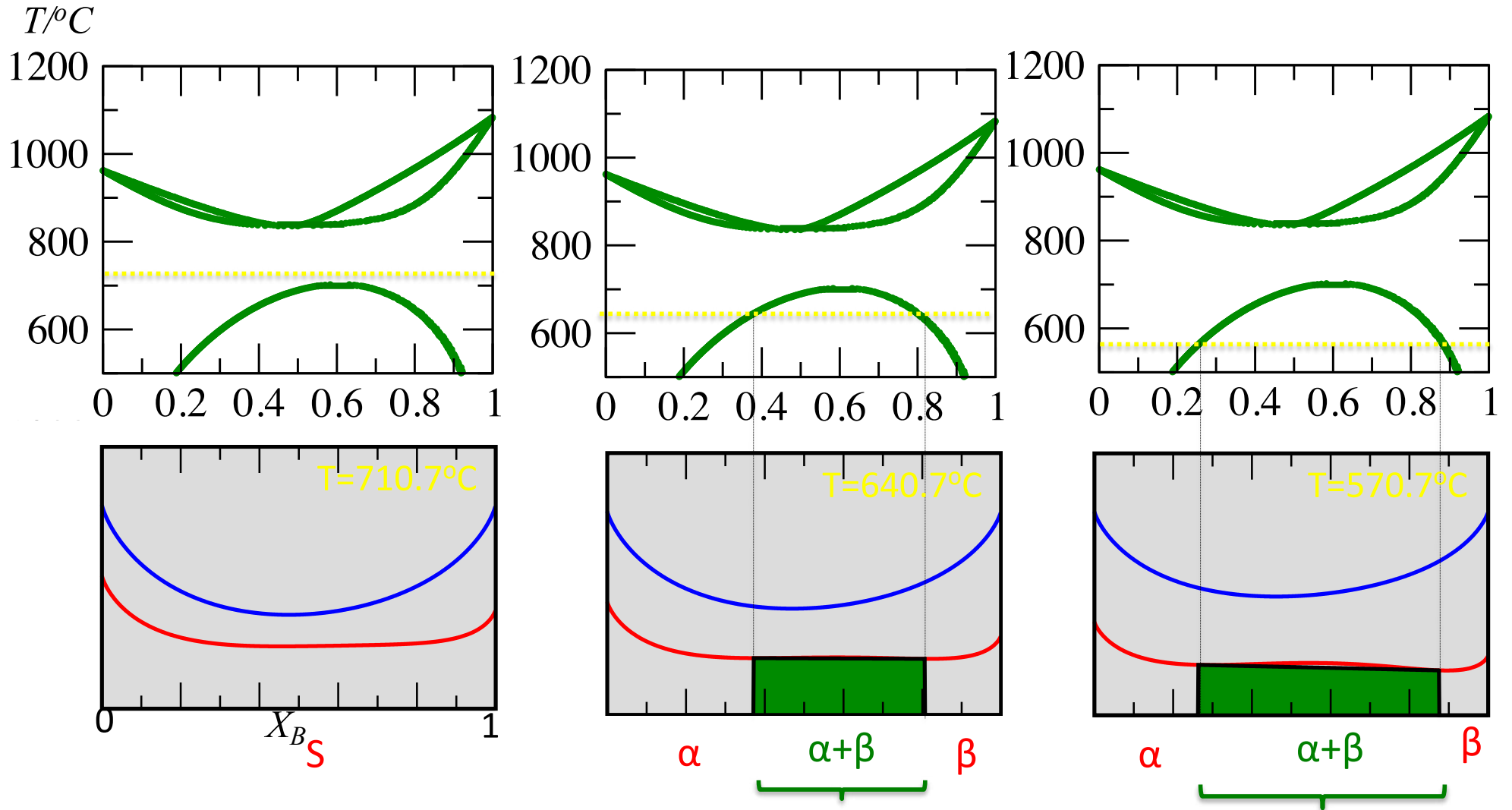


In the following series of graphs (next three slides) the temperature (yellow line) is gradually lowered:



Red: Gibbs free energy of solid
 Blue: Gibbs free energy of liquid





Red: Gibbs free energy of solid
 Blue: Gibbs free energy of liquid

miscibility gap

Mixture of two phases: α and β

miscibility gap

4.) Gibbs free energy for eutectic Ag-Cu system:

Again we use the following expression for the Gibbs free energy:

$$G(T, x_B)/N = \underbrace{x_A \mu_{A,0}(T) + x_B \mu_{B,0}(T)}_{\text{linear term}} + \underbrace{k_B T (x_A \ln x_A + x_B \ln x_B)}_{\text{mixing entropy}} + \underbrace{x_A x_B [a(T) + (x_A - x_B) b(T)]}_{\text{excess enthalpy}}$$

And again, there is a version for the liquid state, $G^L(T, x_B)/N^L$, and a version for the solid state, $G^S(T, x_B)/N^S$.

In the following pictures we take the parameter set appropriate for reproducing the eutectic phase diagram for an Ag-Cu system:

$$N_A [\mu_{A,0}^S(T) - \mu_{A,0}^L(T)] = (-59725 + 48.35 T) \text{ J/mol}$$

$$N_A [\mu_{B,0}^S(T) - \mu_{B,0}^L(T)] = (-75270 + 48.10 T) \text{ J/mol}$$

$$\mu_{A,0}^L(T) = \mu_{B,0}^L(T)$$

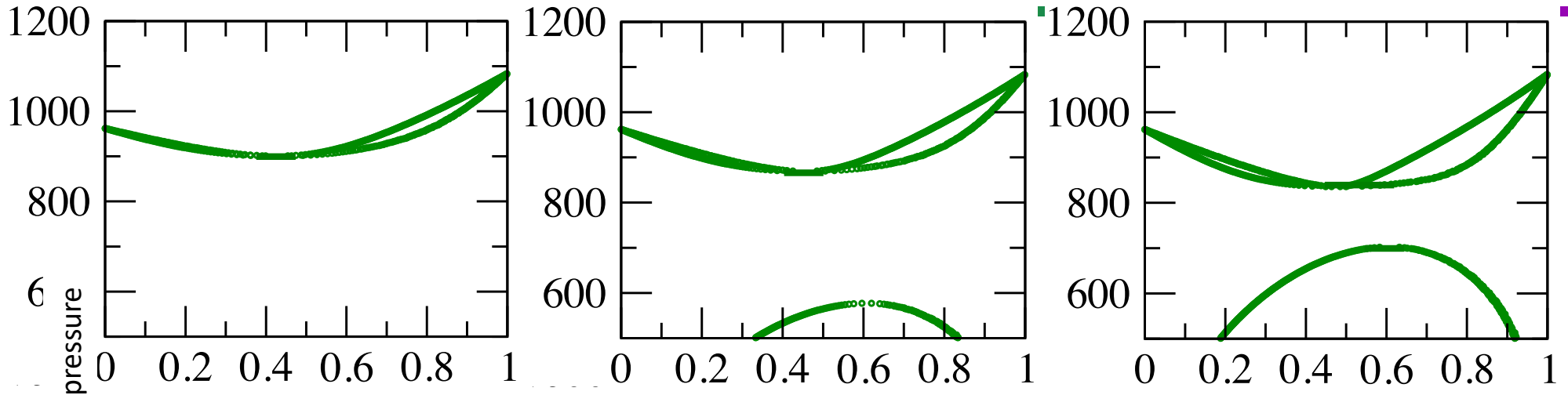
$$N_A k_B = R = 8.314 \text{ J/(mol K)}$$

$$a^S(T) = (34532 - 9.67 T) \text{ J/mol}$$

$$b^S(T) = (-5996 + 1.725 T) \text{ J/mol}$$

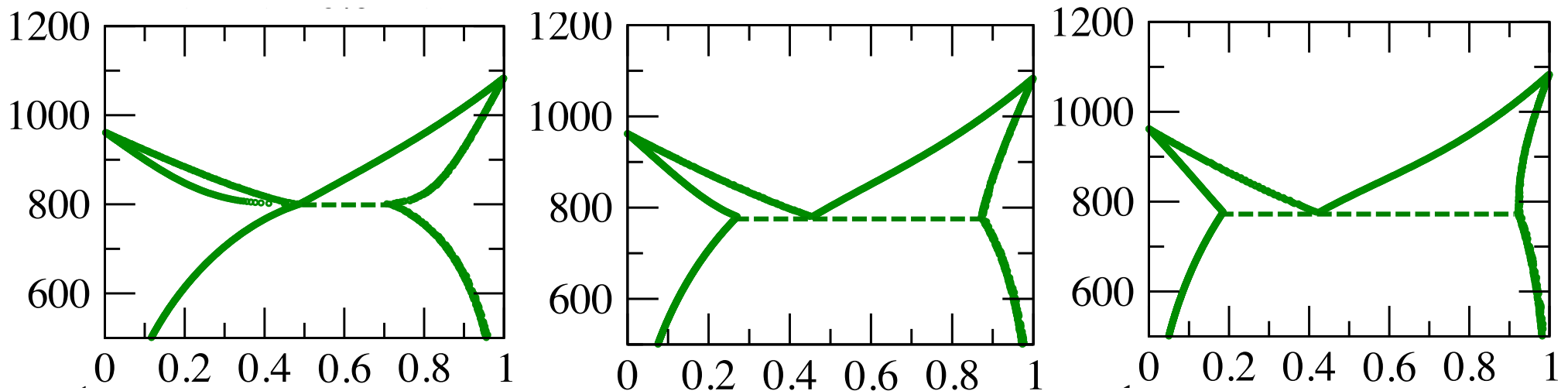
$$a^L(T) = (15171 - 2.537 T) \text{ J/mol}$$

$$b^L(T) = (-2425 + 0.946 T) \text{ J/mol}$$



Transition from ideal to eutectic phase diagram with increasing excess enthalpy

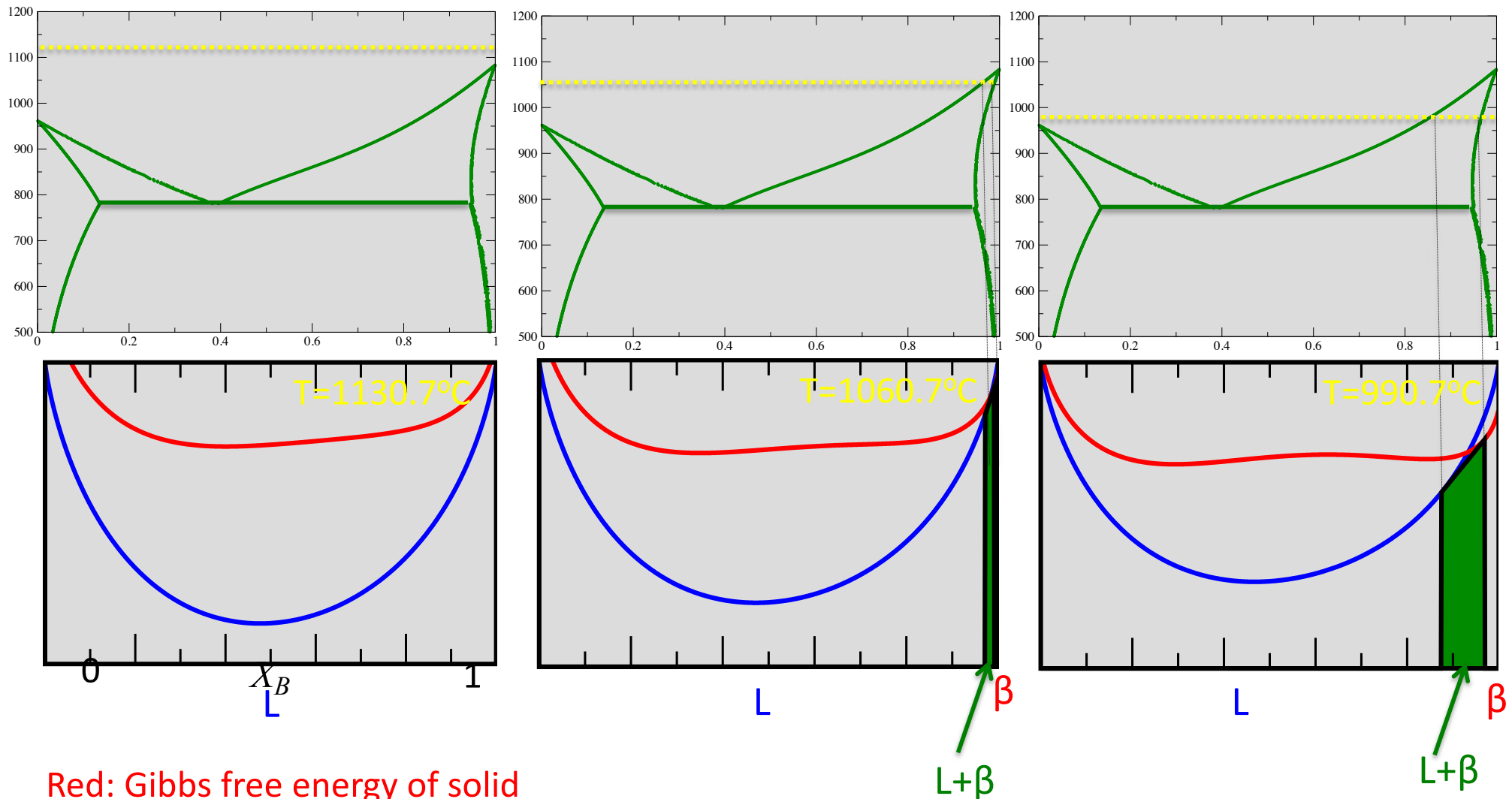
(obtained by scaling the excess enthalpy part of the Gibbs free energy for both solid and liquid by the six factors 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 for the six graphs shown)



4.) Gibbs free energy for eutectic Ag-Cu system:

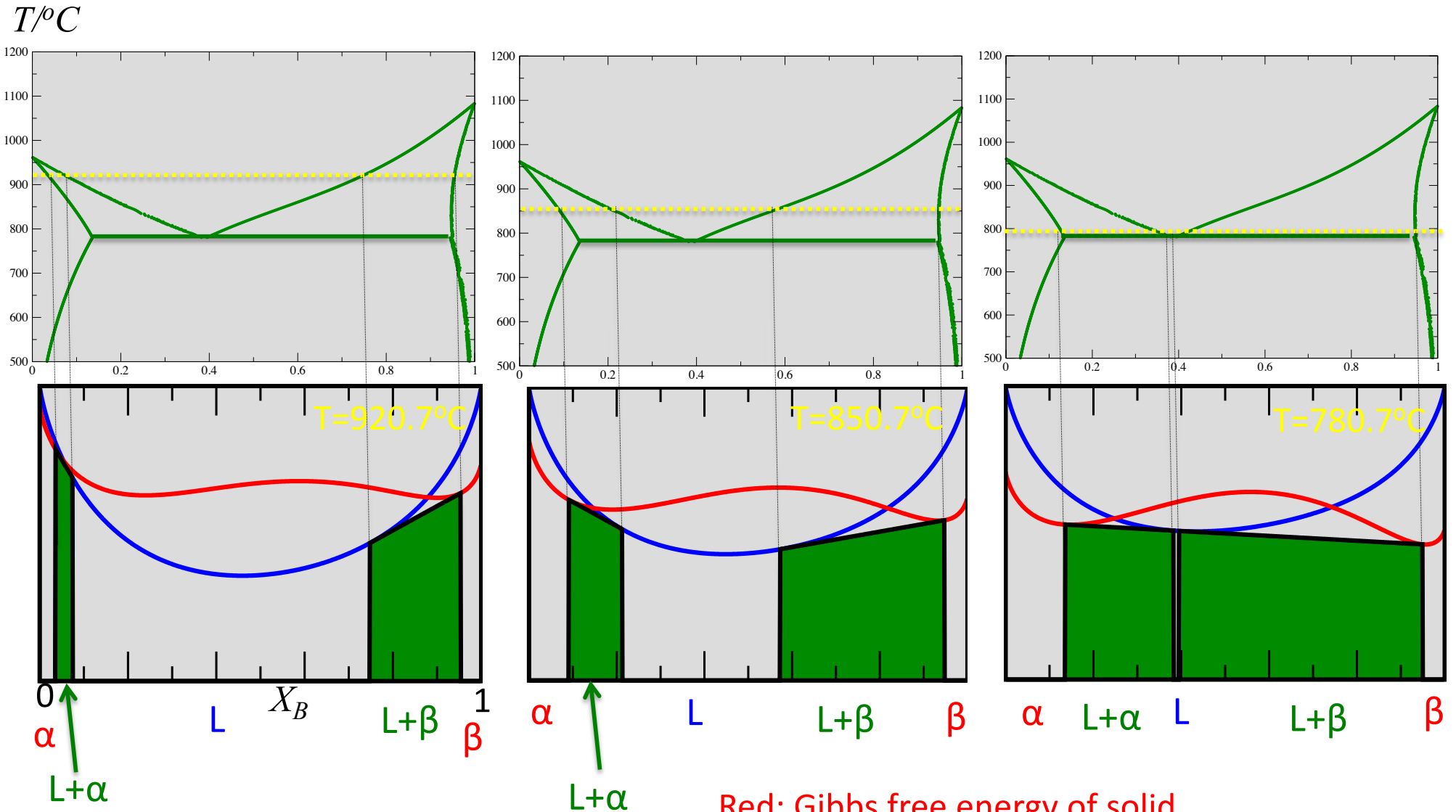
In the following series of graphs (next three slides) the temperature (yellow line) is gradually lowered:

$T/^\circ\text{C}$



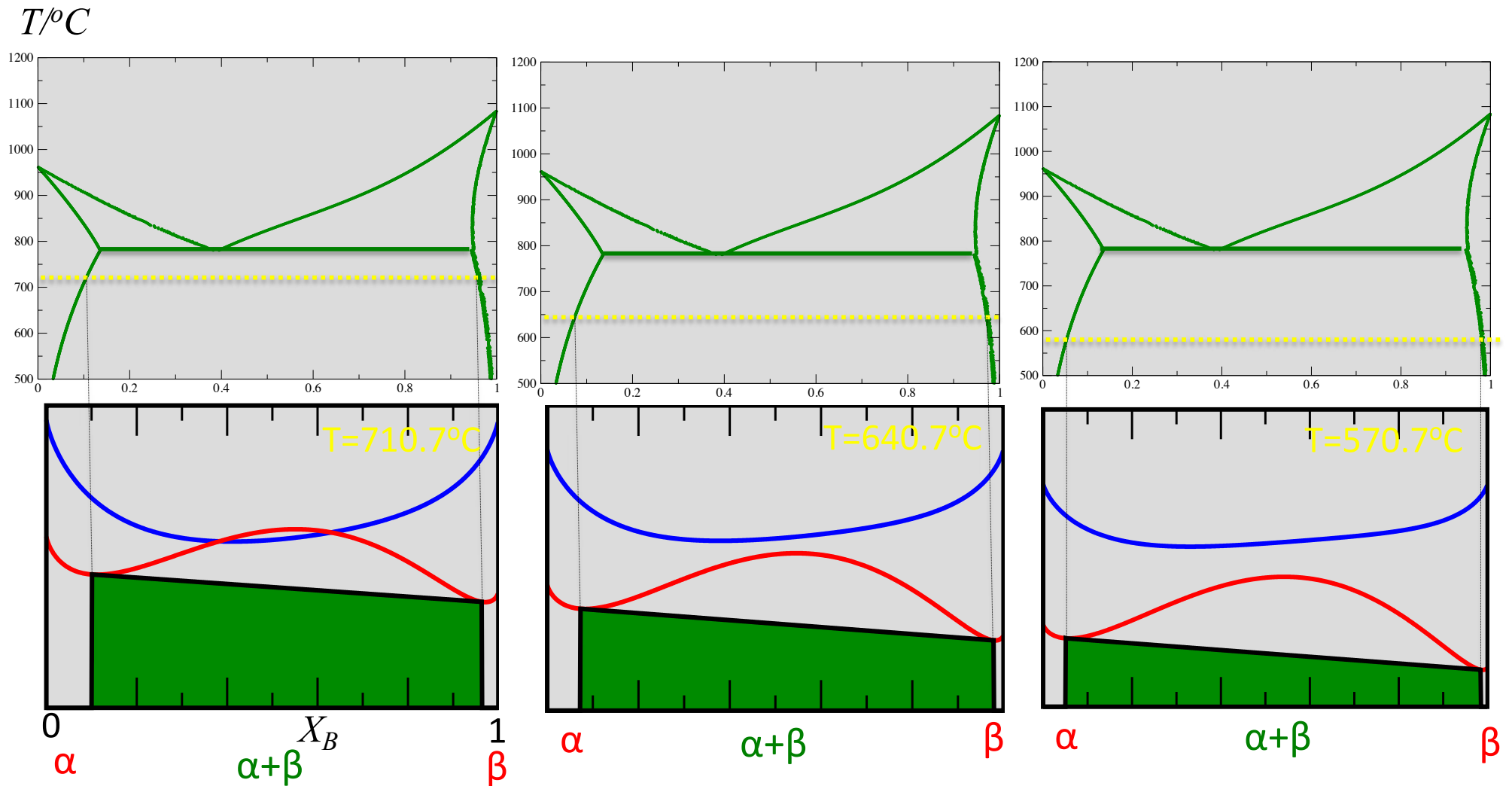
Red: Gibbs free energy of solid
Blue: Gibbs free energy of liquid

Gibbs free energy for eutectic Ag-Cu system:



Red: Gibbs free energy of solid
Blue: Gibbs free energy of liquid

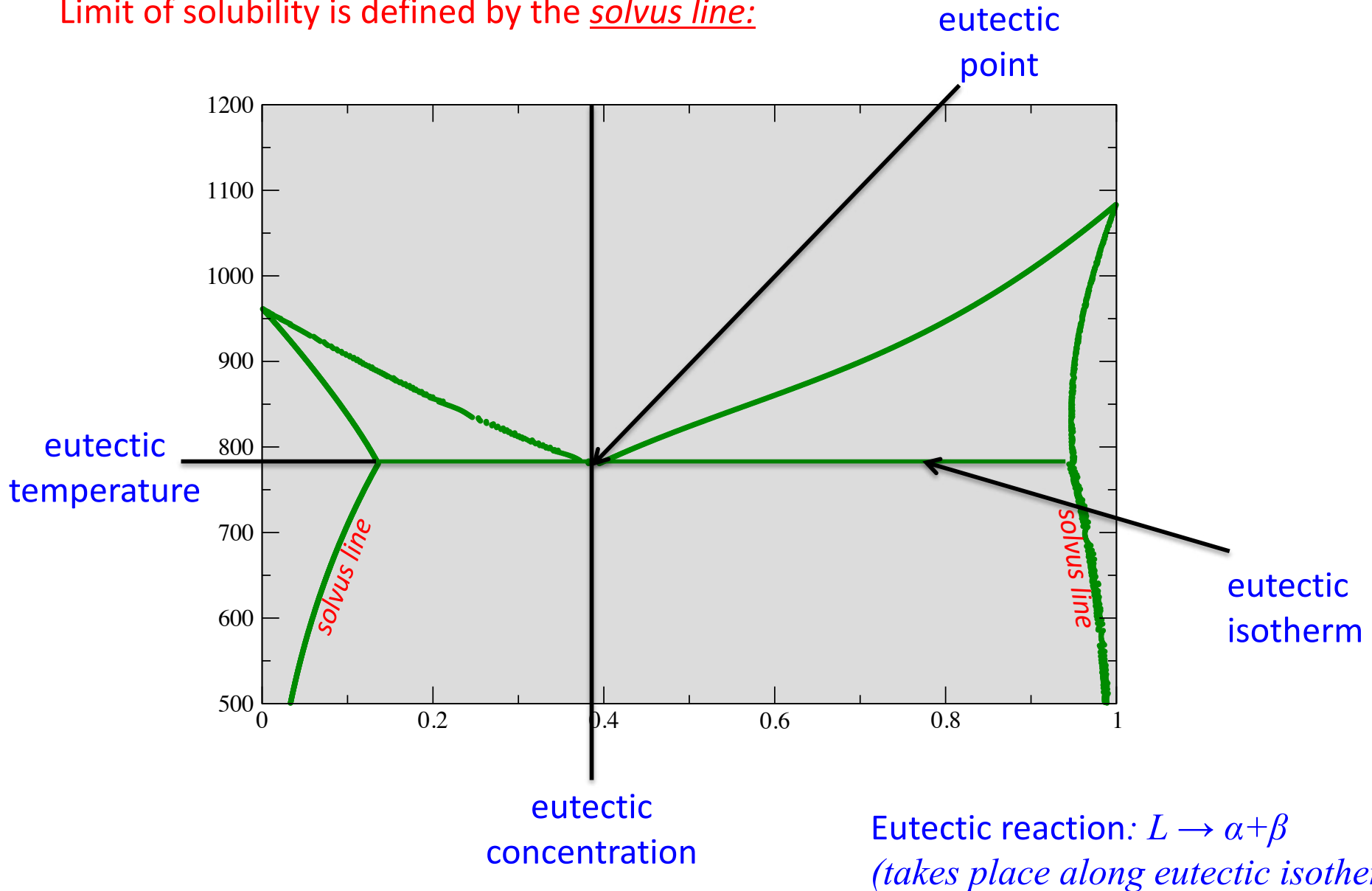
Gibbs free energy for eutectic Ag-Cu system:



Red: Gibbs free energy of solid
 Blue: Gibbs free energy of liquid



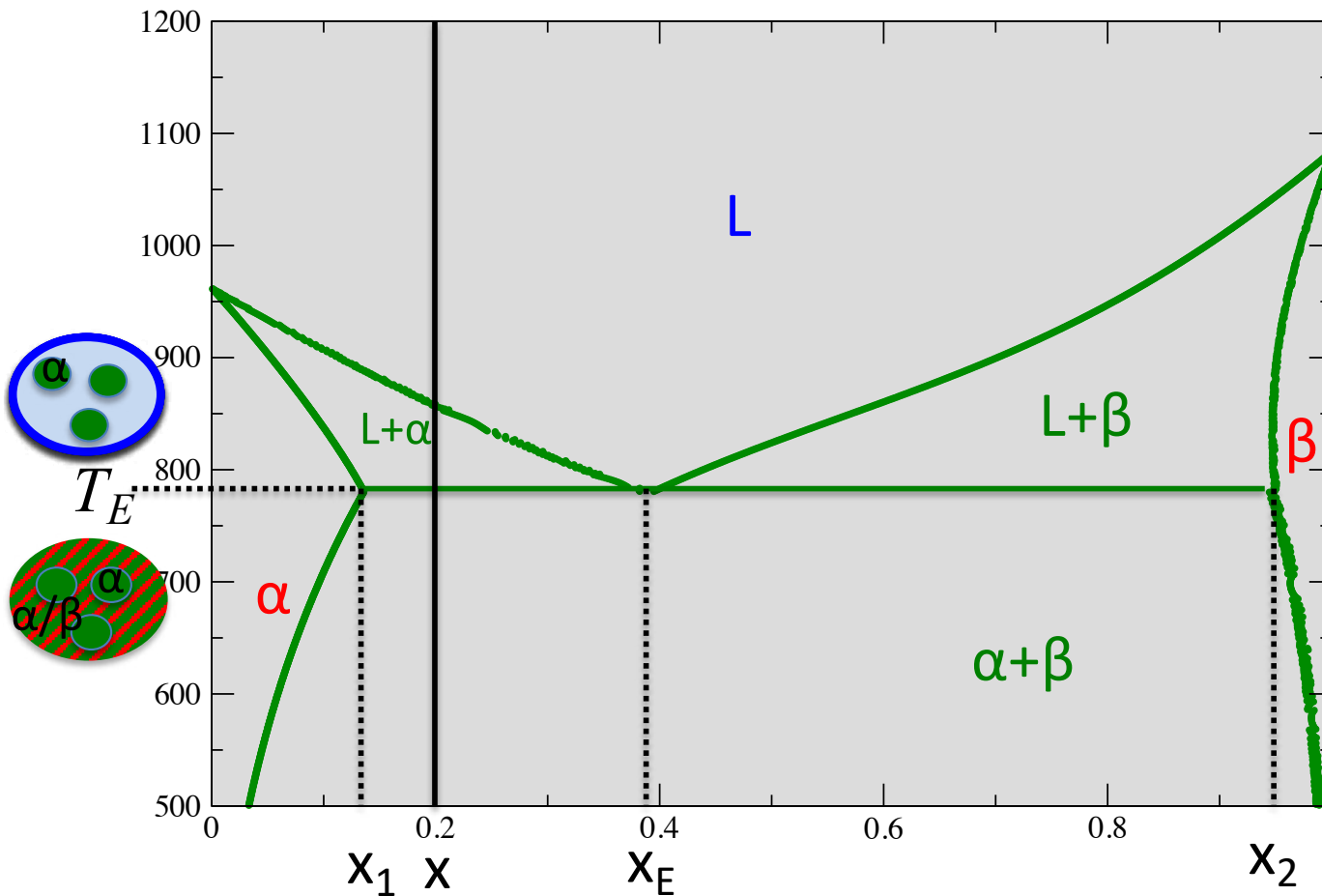
Limit of solubility is defined by the *solvus line*:





Fractions of the phases during eutectic reaction:

Example of how to calculate the fractions when crossing T_E from above using the lever rules:



Just above T_E :

$$\alpha : x_1, \quad w_\alpha = (x_E - x) / (x_E - x_1)$$

$$L : x_E, \quad w_L = (x - x_1) / (x_E - x_1)$$

Just below T_E :

$$\alpha : x_1, \quad w_\alpha = (x_2 - x) / (x_2 - x_1)$$

$$\beta : x_2, \quad w_\beta = (x - x_1) / (x_2 - x_1)$$

In eutectic mixture just below T_E :

$$\alpha : x_1, \quad w_\alpha^E = (x_2 - x_E) / (x_2 - x_1)$$

$$\beta : x_2, \quad w_\beta^E = (x_E - x_1) / (x_2 - x_1)$$

Total α below T_E = primary α formed just above T_E + liquid present just above T_E times fraction of α in eutectic mixture just below T_E : $(x_2 - x) / (x_2 - x_1) = (x_E - x) / (x_E - x_1) + (x - x_1) / (x_E - x_1) * (x_2 - x_E) / (x_2 - x_1)$

$$\text{i.e., } w_\alpha(\text{below } T_E) = w_\alpha(\text{above } T_E) + w_L(\text{above } T_E) * w_\alpha^E(\text{below } T_E)$$

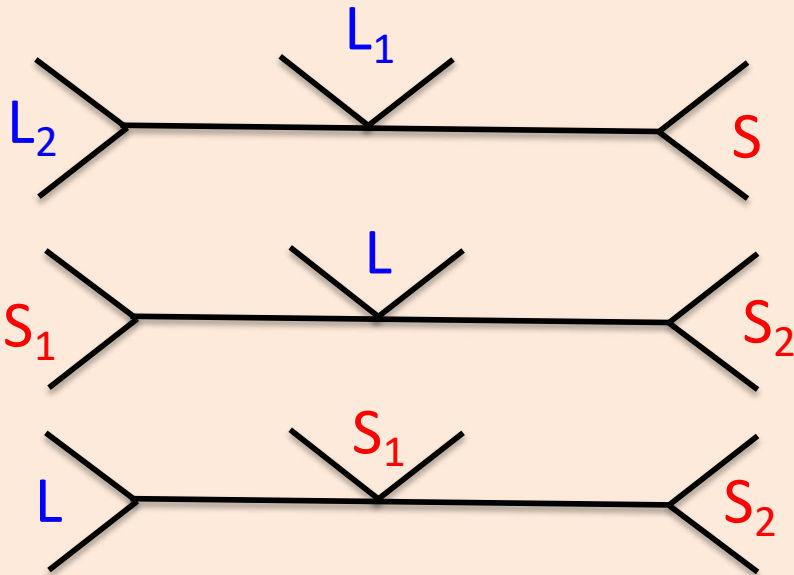


Classification of various types of binary phase diagrams:

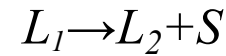
Schematic reaction types at critical lines
 (slopes of phase boundaries can be deformed)

Eutectic type:

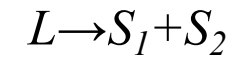
$A \rightarrow B + C$
under cooling



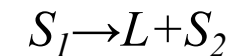
monotectic



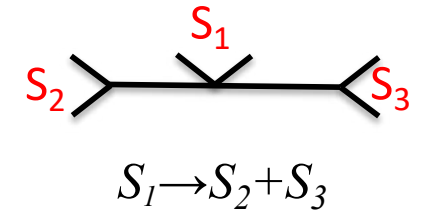
eutectic



catatectic
 (metatectic)

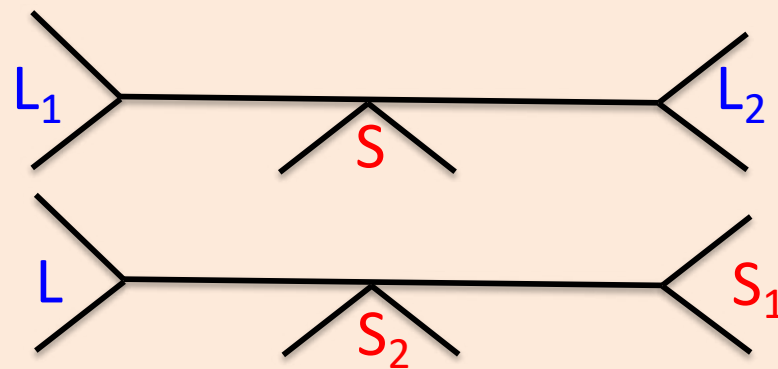


eutectoid:

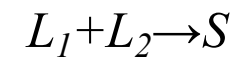


Peritectic type:

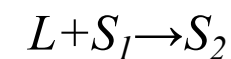
$A + B \rightarrow C$
under cooling



syntectic



peritectic



peritectoid:

