METALS FOR SUSTAINABLE MANUFACTURING

Thermodynamics and phase diagrams

MAURO PALUMBO

mauro.palumbo@unito.it
Dipartimento di Chimica
Università di Torino
Via Pietro Giuria 9 –10125 Torino

Recap: thermodynamics

Thermodynamics is a branch of physics that ***deals with the relationships between heat and other forms of energy, and the laws governing the conversion of energy from one form to another***. It involves the study of the effects of changes in temperature, pressure, and volume on physical systems at the macroscopic scale.

Thermodynamics applies to a wide variety of topics in science and engineering, such as engines, ***phase transformations***, chemical reactions, and the behavior of materials under thermal stress. It plays a crucial role in understanding the efficiency of energy conversion processes and the fundamental properties of matter.

Recap: terminology

- **Component:** elements or chemical compounds (e.g. Fe, Ni, CH4)
- **Phase:** portion of a system with homogeneous properties and composition (liquid, fcc)
- **System:** mixture of one or more phases (e.g. perlitic steel, boiling water)

The thermodynamic properties of a system depend on:

- **Temperature** (T)
- **Pressure** (P)
- **Composition** (n_i, X_i, etc.)

The relative stability of a system is determined by **the Gibbs free energy (G):**

$$G = H - TS$$

Recap: terminology

Other state functions exist, but typically are less useful

Table 2.1 *State functions having an extremum at equilibrium, if the characteristic state variables are kept constant*

Name	Symbol or definition	Characteristic state variables		
Entropy	S	U	V	N_i
Massieu's function	$\Psi = S - U/T$	$1/T$	V	N_i
Planck's function	$\Phi = S - U/T - p \cdot V/T$	$1/T$	p/T	N_i
Internal energy	U	S	V	N_i
Enthalpy	$H = U + p \cdot V$	S	$-p$	N_i
Helmholtz free energy	$F = U - T \cdot S$	T	V	N_i
Gibbs energy	$G = U + p \cdot V - T \cdot S$	T	$-p$	N_i
Grand potential	$-p \cdot V = U - T \cdot S - \sum_i \mu_i \cdot N_i$	T	V	μ_i
Gibbs–Duhem equation	$0 = U + p \cdot V - T \cdot S - \sum_i \mu_i \cdot N_i$	T	p	μ_i

- **G is the most useful in chemistry and metallurgy** because we can control T and P.
- In condensed states (liquids and solids), **variations of P are small** (P≈constant).

Recap: terminology

The integral free energy G is often normalized per mole of phase:

$$G_m = \frac{G}{N}$$

G_m	Molar free energy
G	Free energy of the system
N	Number of moles of the system

A system may contain one (homogenous) or more phases (heterogenous). In the latter case, the integral free energy G is expressed as:

$$G = \sum_{\varphi} N_{\varphi} G^{\varphi}$$

G^{φ}	Free energy of the phase φ
N_{φ}	Number of moles of the phase φ

The composition is often expressed in terms of molar fractions X_i :

$$X_i = \frac{n_i}{n_{tot}}$$

n_i	Number of moles of component i
n_{tot}	Total number of moles in the system

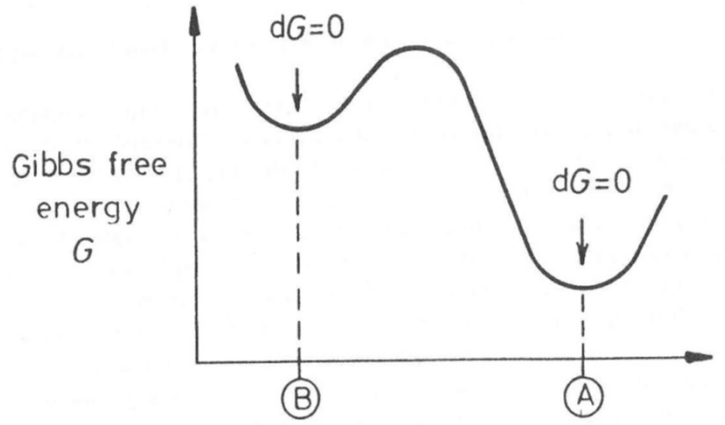
Recap: terminology

For a given system in the condensed state, equilibrium is described by making use of the Gibbs free energy as a function of *T, P, mole fraction, …*

$$dG = -SdT + VdP + \sum_i \mu_i dn_i + ...$$

In an isothermal isobaric system with constant amounts of all components**, the equilibrium is reached when the Gibbs energy reaches its minimal value**.The equilibrium condition is expressed by G = min or

$$dG = 0 \qquad \text{and} \qquad d^2G \geq 0$$



It will be employed at *T* and/or *P* and/or *mole fraction* = const. Local minima are *metastable states.*

The integral quantity, G, can be made explicit when a reference state is defined.

Recap: reference states

Reference states are used as baseline conditions from which changes in thermodynamic functions, such as enthalpy (H), internal energy (U), and Gibbs free energy (G), are measured or determined from thermodynamic equations. These reference states are necessary because absolute values of these functions cannot be directly evaluated; only changes in these values are physically meaningful and can be determined.

A reference state is a set of conditions (including temperature, pressure, and sometimes composition) that is arbitrarily chosen and universally accepted for a particular substance. From this reference point, the changes in thermodynamic properties can be calculated when the substance undergoes a process or a reaction.

A typical choice is the **Standard Element Reference state (SER) in which H_{298} = 0 and S = S_{298} for the phase stable at 298 K and 1 bar for the stable phase.** S_{298} is the absolute entropy at 298 K calculated from S=0 at 0 K (see note below). For example, for pure Fe, SER is the bcc phase with H=0 and S=S_{298}(bcc).

However, other choices are possible and equally correct (and sometimes more convenient).

Note: an exception is the entropy. Because of the third principle of thermodynamics, at 0 K for a perfect solid S=0. So we can define an absolute entropy, for example at 298 K (S_{298})

Single component systems

Let us consider a system made of a single component which can occur in different phases. In order to establish which phase is stable at a given T and *p,* their free energy, G, must be compared.

For each phase: G = H – TS. H and S can be obtained from (at constant P, typically P=1 bar):

$$H = H_{ref} + \int_{ref}^{T} C_p dT \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

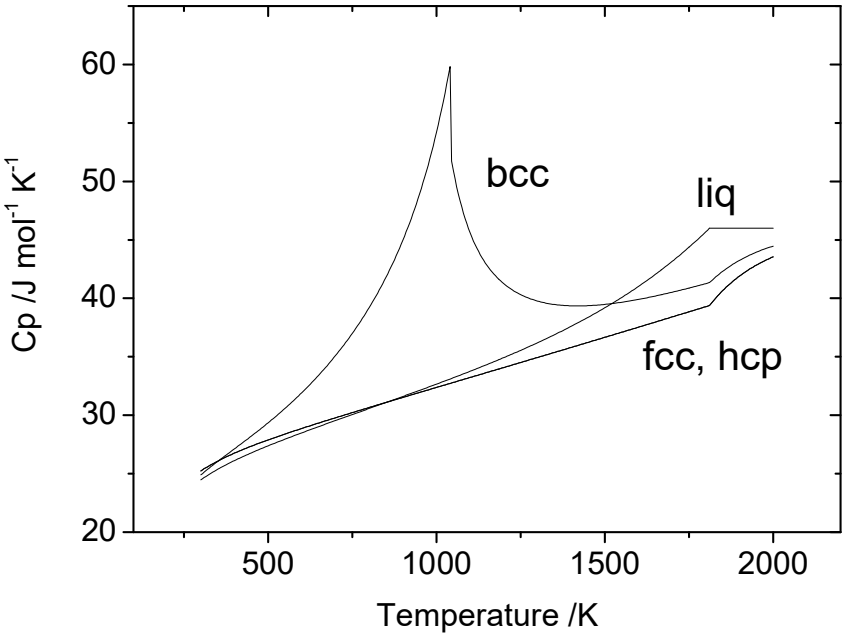
$$S = S_{ref} + \int_{ref}^{T} C_p d\ln T \qquad \frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

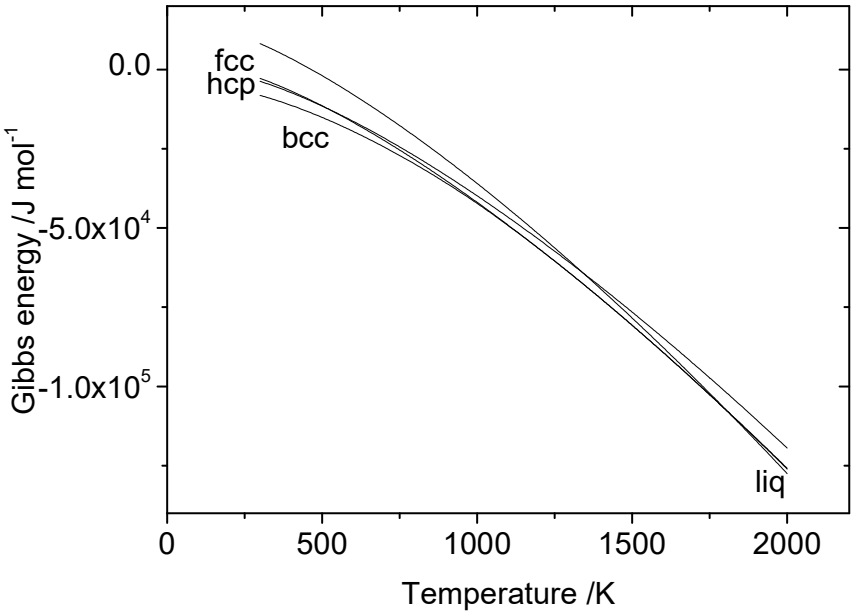
Experimental data are typically available for C_P and these data are fitted by:

$$C_p = c_1 + c_2 T + c_3 T^2 + c_4 / T^2 + \ldots + C_{p,mag} + \ldots$$

C_1, c_2, etc. are obtained from fitting.

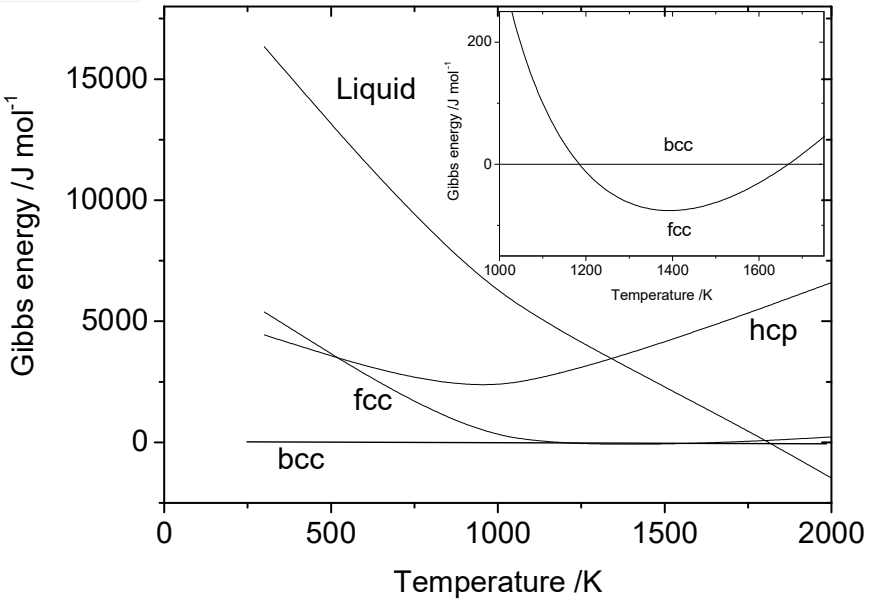
An example: the element Fe





Specific heat and free energies of ***fcc, bcc, hcp and liquid*** phases at P=1 bar relative to ***SER***.

An example: the element Fe

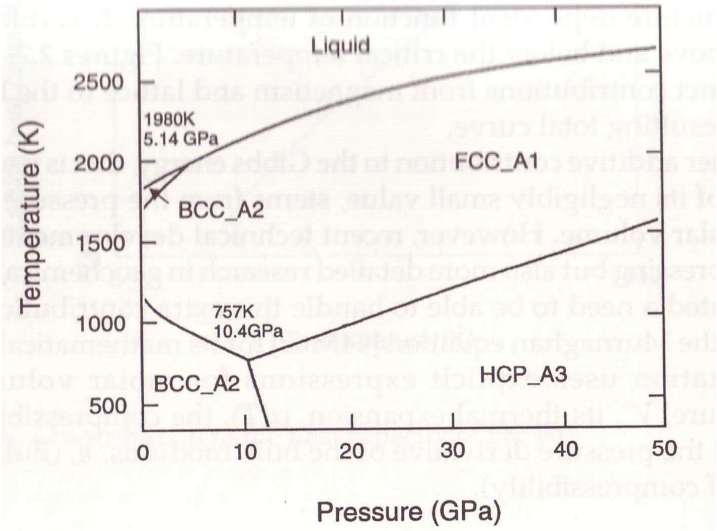


Free energies of ***fcc, hcp and liquid phases*** relative to ***bcc*** phase for Fe at *p* = 1 bar.

p-T phase diagram

Gibbs phase rule:

$v = c - f + 2$



In materials science, often p=const=1 bar

Driving force for solidification (pure elements)

In phase transformations, often we deal with differences in free energy at T away from equilibrium.

Example: liquid metal undercooled by ΔT below T_m before it solidify (P=1 bar).

$$\Delta H = H_L - H_s$$
$$\Delta S = S_L - S_s$$
$$\Delta G = \Delta H - T\,\Delta S$$

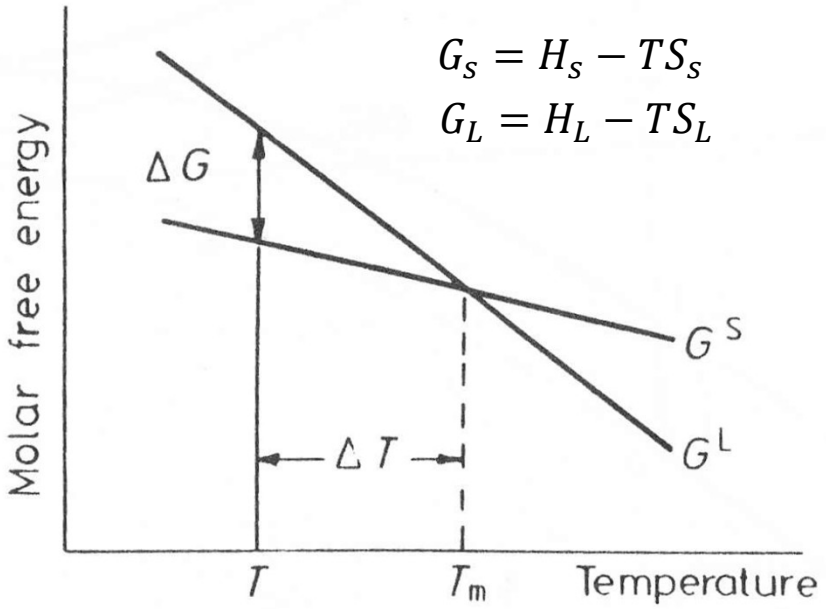
At T_m:

$$\Delta G = \Delta H - T_m\,\Delta S = 0$$

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$

$\Delta H = L$: latent heat of fusion

$\Delta S = \frac{L}{T_m}$: entropy of fusion (approx. constant =R)



$$\Delta G \approx L - T\frac{L}{T_m} \approx \frac{L\Delta T}{T_m}$$

Approx. driving force for solidification (for small ΔT)

Binary systems

Most metallic materials are alloys. Hence, we need to describe the thermodynamics of binary systems (2 components) and more generally multicomponent systems.

When we mix two components A and B, two possibilities can occur:

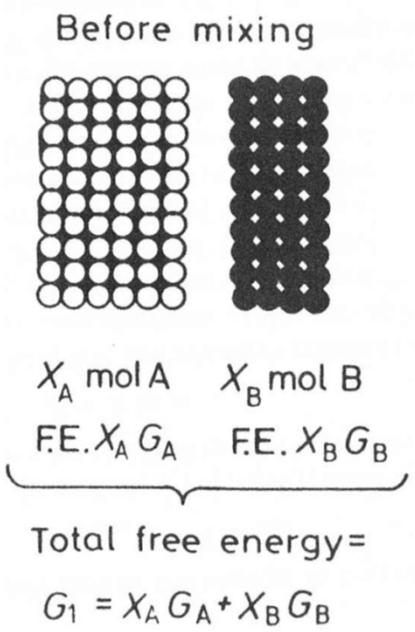
- The two components *A and B have the same crystal structure* and they form a **substitutional solid solution** with the same crystal structure. These are **homogeneous systems**.
- The two components *A and B have different crystal structures* (**heterogenous systems**). Both crystal structures can form substitutional solid solutions.

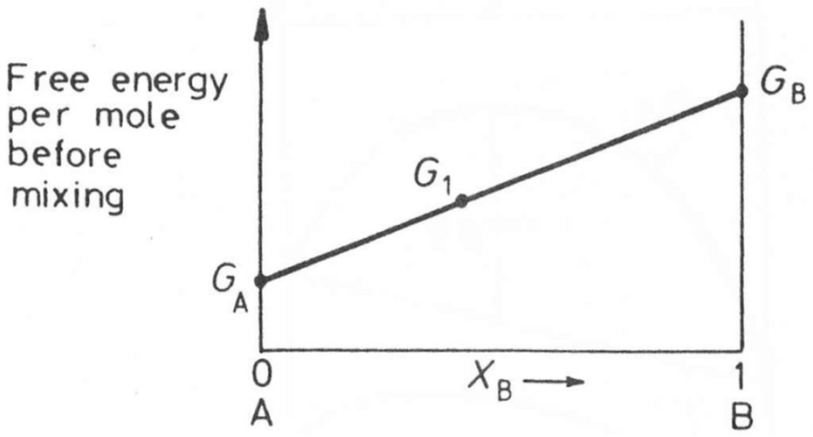
Other possibilities are:

- The formation of **interstitial solid solutions**.
- The formation of different phases with a crystal structure which is not as A neither as B

Gibbs energy of phases in binary systems
Substitutional solid solutions: 2 components, one phase

For simplicity, we take a system containing in total one mole of A and B (in total)



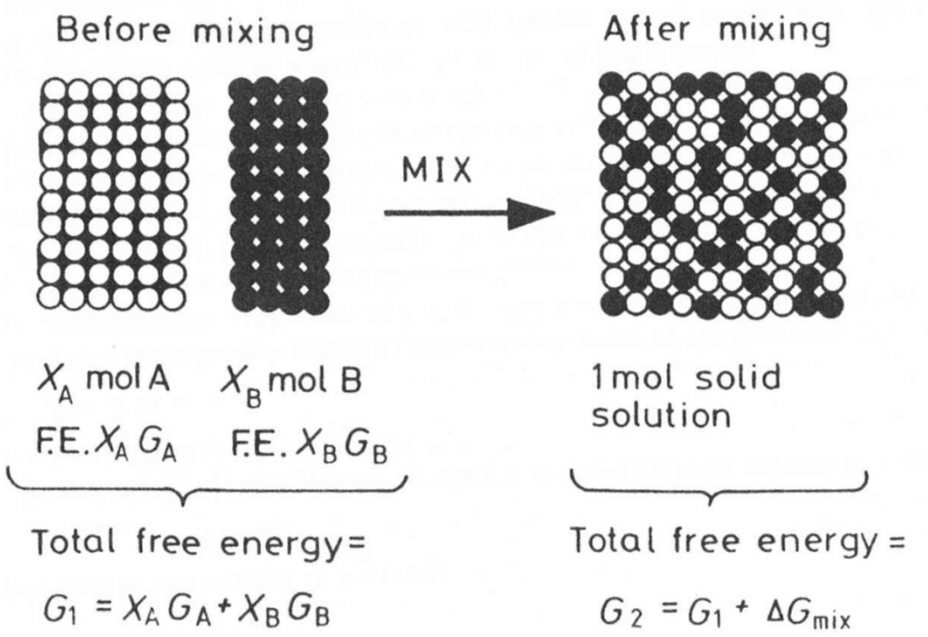


$G_{A,}$ G_B → molar free energies of pure elements A and B

$X_{A,}$ X_B → molar fractions A and B

G_1 is the Gibbs energy of the unreacted mixture, it is equal to the weighted sum of the free energies of the pure elements

Gibbs energy of phases in binary systems
Substitutional solid solutions: 2 components, one phase



After mixing, the molar free energy of the system is G_2 which includes G_1 plus a "**mixing free energy**" ΔG_{mix}.

We can also define a "**mixing enthalpy**" ΔH_{mix} and a "**mixing entropy**" ΔS_{mix}.

The thermodynamics of mixing depends on these quantities and we need to determine them.

$$G_1 = H_1 - TS_1$$
$$G_2 = H_2 - TS_2$$

$$\Delta H_{mix} = H_2 - H_1$$
$$\Delta S_{mix} = S_2 - S_1$$

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

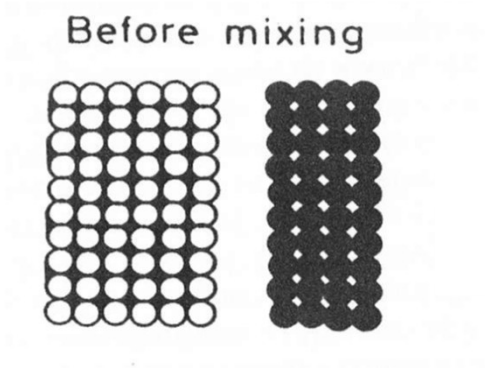
Ideal solutions: entropy of mixing

The simplest possible type of solution is **an ideal solution, i.e. one with zero mixing enthalpy and only configurational mixing entropy.** The latter can be easily evaluated from statistical thermodynamics, i.e. Boltzmann equation for entropy:

$$S = k_B \, ln \, \omega_{conf}$$

k_B is Boltzmann constant

ω_{conf} is the number of distinguishable configurations in the system



Before mixing, only one possible distinguishable configuration:

$$S_1 = k_B \, ln \, 1 = 0$$

So: $\Delta S_{mix} = S_2$

Ideal solutions: entropy of mixing

After mixing, assuming that all configurations of A and B atoms are equally probable, the number of distinguishable ways of arranging the atoms on the atomic sites is

$$\omega_{config} = \frac{(N_A + N_B)!}{N_A!\, N_B!}$$

N_A and N_B are the number of A and B atoms, respectively

For 1 mol of solid solution: $N_A = X_A N_a$ $N_B = X_B N_a$
(N_a is Avogadro's number)

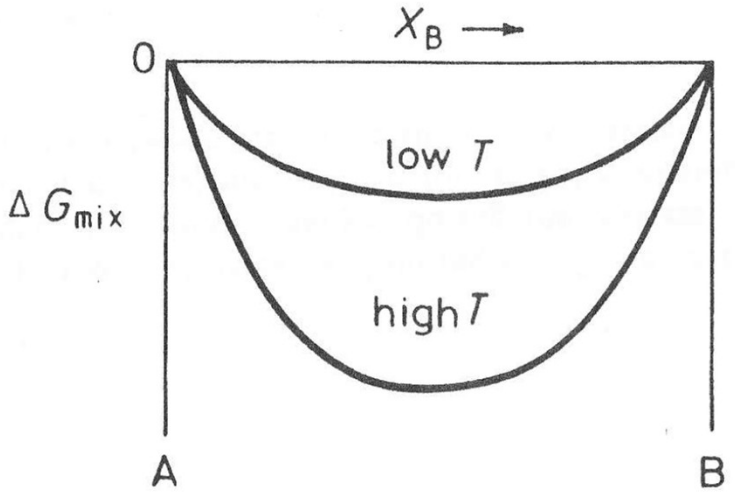
Remembering Sterling's approximation (for large N): $\ln N! \approx N ln N - N$

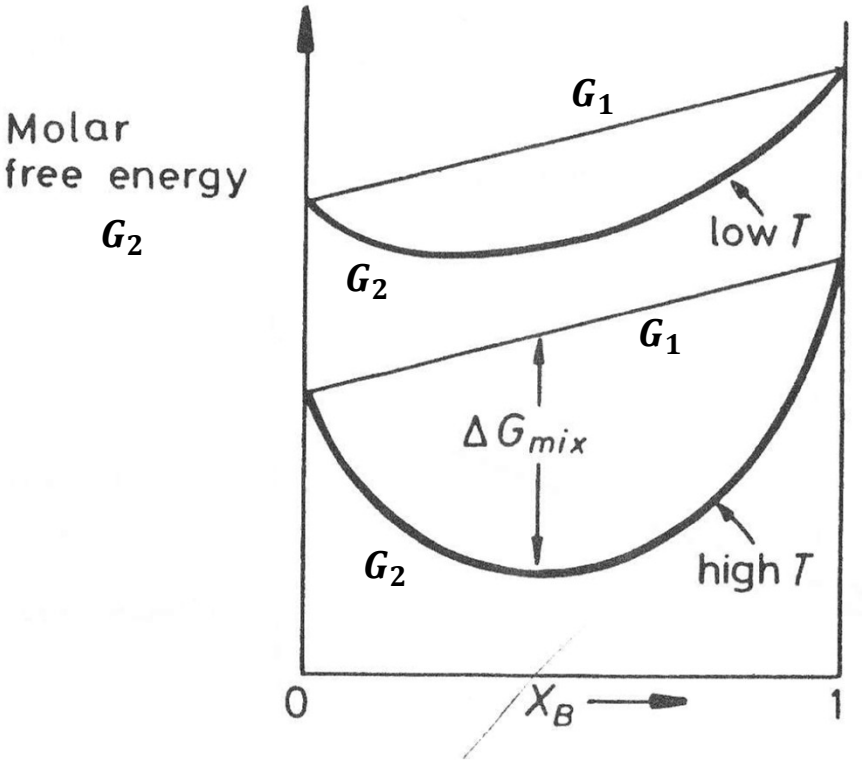
$$\Delta S_{mix} = S_2 = k_B \, ln \, \omega_{config} = k_B ln \frac{(N_A+N_B)!}{N_A! N_B!} = \cdots = -R \, (X_A ln X_A + X_B ln X_B)$$

Ideal solutions

$$\Delta H_{mix} = 0 \qquad \Delta S_{mix} = -R(X_A ln X_A + X_B ln X_B)$$

$$\Delta G_{mix} = RT(X_A ln X_A + X_B ln X_B)$$





Regular solutions

Only a few real solutions behave like ideal solutions. Regular solutions are slightly more complex. In a regular solution, **the mixing enthalpy is proportional to the molar fractions and the mixing entropy is the same as in ideal solution (configurational).**

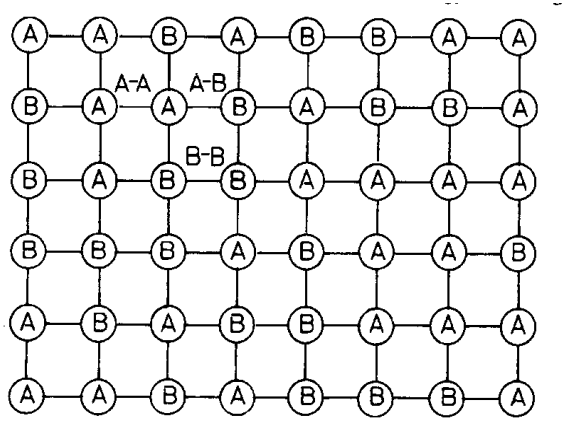


Fig. 1.13 The different types of interatomic bond in a solid solution.

Assumptions:

- *bonding energies do not change with composition*
- *P and V remain constant when mixing (hence $\Delta U = \Delta H$)*

A—A bonds each with an energy ε_{AA},
B—B bonds each with an energy ε_{BB},
A—B bonds each with an energy ε_{AB}.

Regular solutions

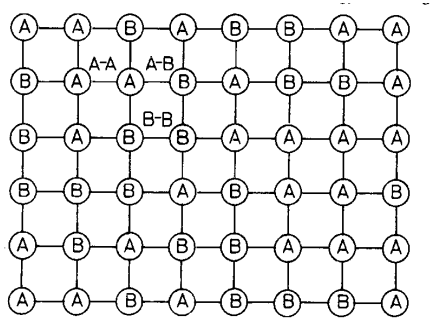


Fig. 1.13 The different types of interatomic bond in a solid solution.

$$U = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB}$$

P_{AA}, P_{BB}, P_{AB} → n. of bonds AA, BB, AB, respectively

$$N_A = \frac{P_{AB}}{z} + 2\frac{P_{AA}}{z}$$

$$N_B = \frac{P_{AB}}{z} + 2\frac{P_{BB}}{z}$$

N_A, N_B → n. of atoms A and B, respectively, in the lattice

z → coordination number of the lattice

Regular solutions

$$P_{AA} = \frac{1}{2}(zN_A - P_{AB}) \qquad P_{BB} = \frac{1}{2}(zN_B - P_{AB})$$

$$U = \frac{1}{2}zN_A\varepsilon_{AA} + \frac{1}{2}zN_B\varepsilon_{BB} + P_{AB}\left(\varepsilon_{AB} - \frac{1}{2}\varepsilon_{AA} - \frac{1}{2}\varepsilon_{BB}\right)$$

$$\Delta U_{mix} = P_{AB}\left(\varepsilon_{AB} - \frac{1}{2}\varepsilon_{AA} - \frac{1}{2}\varepsilon_{BB}\right) = P_{AB}\varepsilon = \Delta H_{mix}$$

$$P_{AB} = N_a X_A z X_B$$

N_a → Avogadro number

$N_a X_A$ → number of lattice sites occupied by A atoms

zX_B → prob. that around a given lattice site there is a B atom

$$\Delta H_{mix} = X_A X_B z N_a \varepsilon$$

$$\Omega = N_a z\, \varepsilon$$

The regular solution parameter Ω depends on the bonding energies and z

Regular solutions

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

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

$$\Delta G_{mix} = RT(X_A ln X_A + X_B ln X_B) + \Omega X_A\, X_B$$

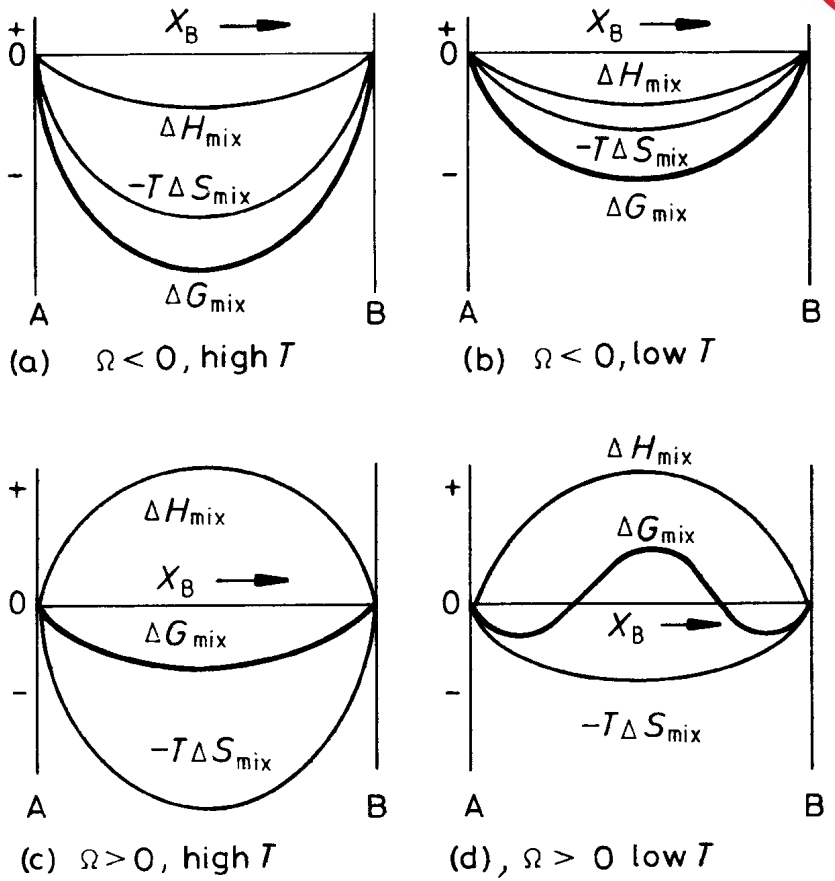
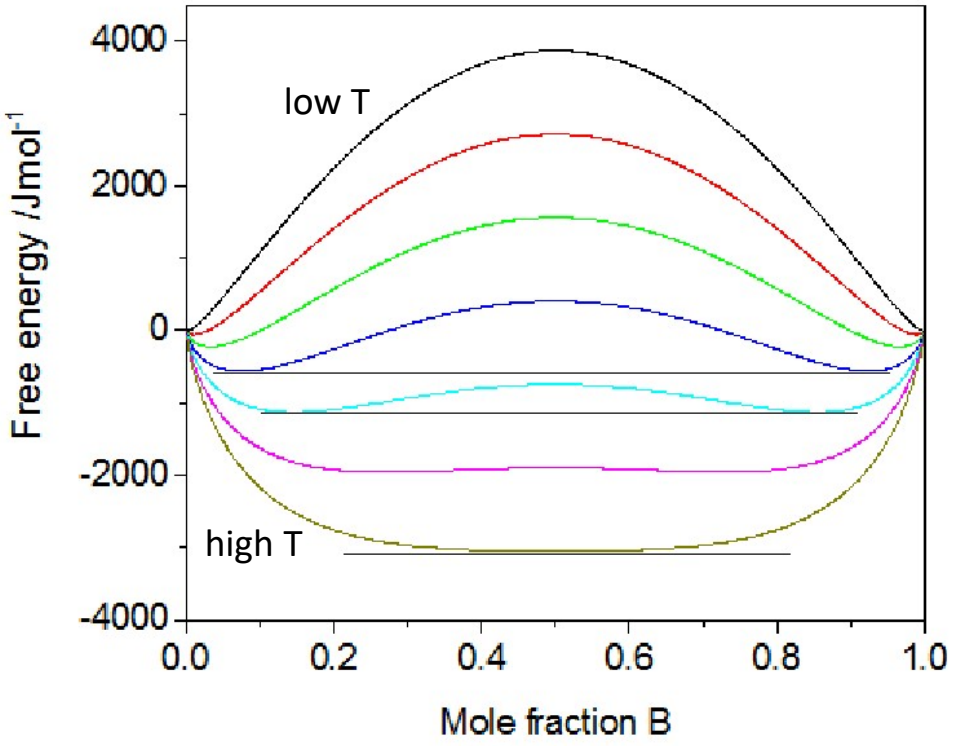


Fig. 1.15 The effect of ΔH_{mix} and T on ΔG_{mix}.

Miscibility gaps



Free energies at T from 500 K to 1700 K at 200 K interval with $\Omega = 27000$ Jmol^{-1}.

At low T, **a miscibility gap is present**, i.e. **two solid solutions with the same structure but different compositions appear** (two tangent points from the common tangent construction, see next slides).

Solubility may become complete above a critical temperature (one tangent point).

Quenching from high temperature may force (non-equilibrium) solubility.

Real solutions

$$\Delta H_{mix} = complex\ equations$$

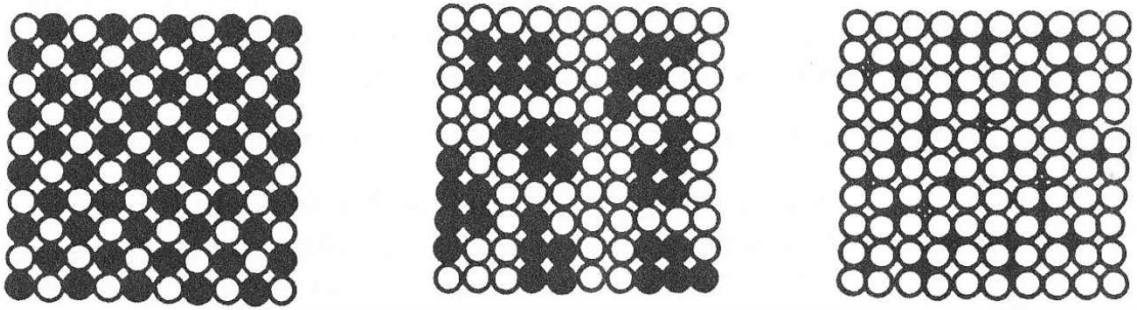
Some (a few) real solutions behave like regular solutions, but most of them are more complex and require more complex models.

ΔH_{mix} depends on temperature and composition in a complex way

Bonding energies depend on composition and P and V do not remain constant during mixing.

Several more complex models are available (not described in this course).

When atomic sizes are very different, we obtain *interstitial solutions*.



Chemical potentials in binary systems

Chemical potential of A in a binary system with A and B components

$dG' = \mu_A dn_A$ P, T, n_B constants $\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B}$

In general:

$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$

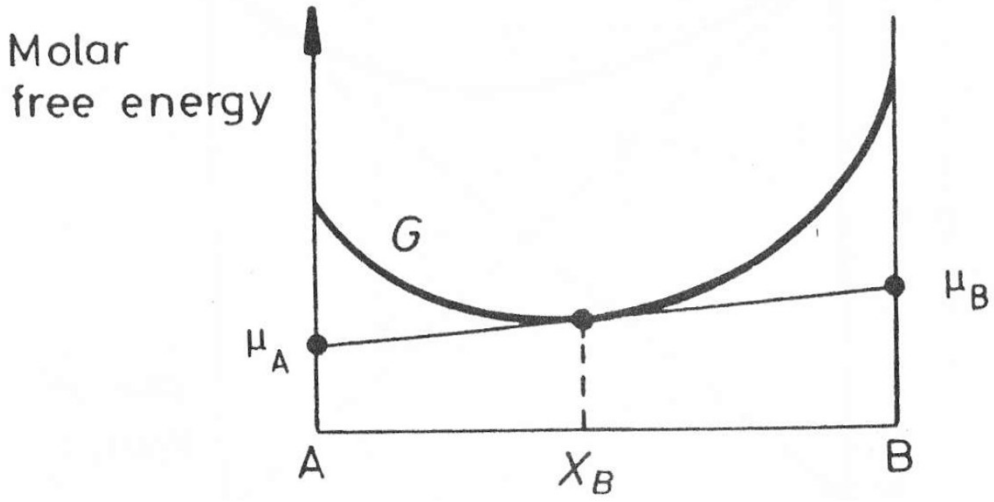
(G' is the Gibbs free energy of the system, not the molar Gibbs energy)

Chemical potentials **in ideal solutions**:

$G = \mu_A X_A + \mu_B X_B$

$\mu_i = G_i + RTlnX_i$

G is the molar Gibbs free energy

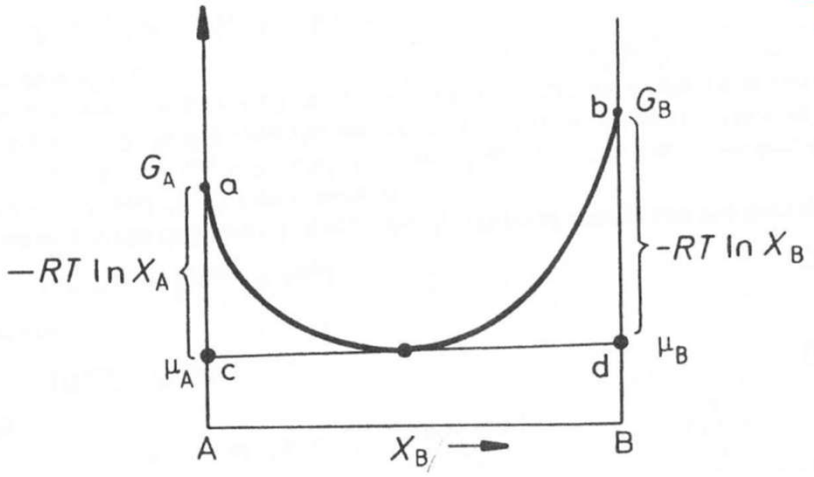


Chemical potentials in binary systems

Chemical potentials **in ideal solutions**:

$$\mu_A = G_A + RTlnX_A$$

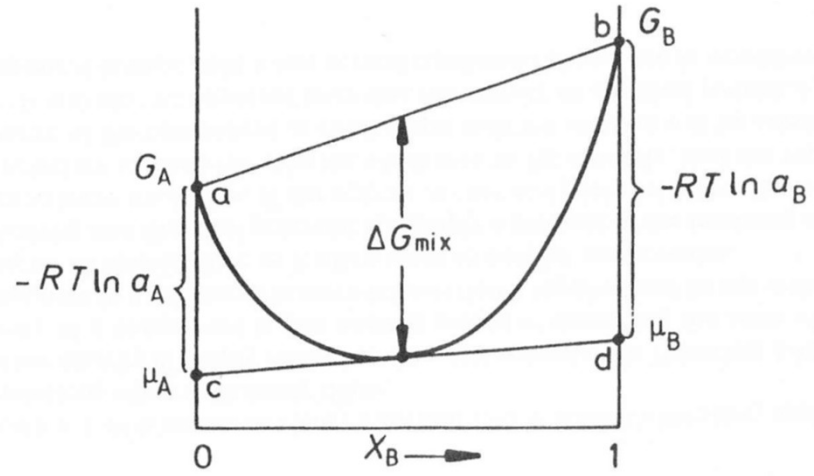
$$\mu_B = G_B + RTlnX_B$$



Chemical potentials **in real solutions**:

$$\mu_A = G_A + RTlna_A$$

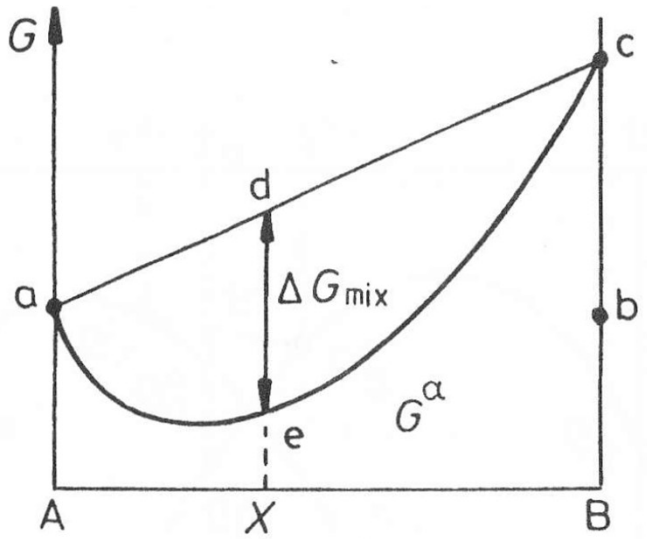
$$\mu_B = G_B + RTlna_B$$

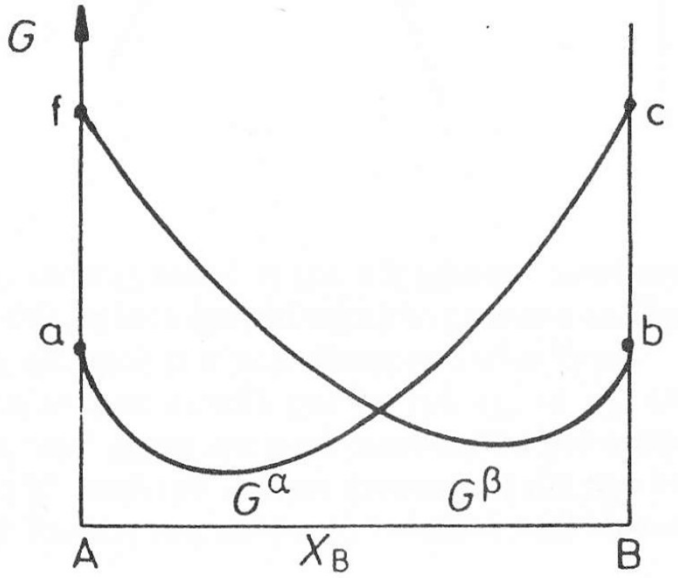


Heterogeneous binary systems

Often components A and B do not have the same crystal structure at the certain T. For example, **A is stable in the α structure and B in the β structure, where α could be bcc and β could be fcc.**

We need to consider **two free energy curves (G_α and G_β) for two possible solid solutions as a function of composition (at a given T)**.





Heterogeneous binary systems

At certain compositions, **the free energy of the system can be minimized by forming a mixture of the α and β phases.**

Mathematically, the minimum of the free energy in a heterogeneous equilibrium is equivalent to having **each component with the same chemical potential in each phase, i.e.**

$$\mu_A^\alpha = \mu_A^\beta \qquad \mu_B^\alpha = \mu_B^\beta$$

There is also an equivalent **geometrical construction (common tangent method**, next slide) which is sometimes easier to understand and use (at least in binary systems).

In binary heterogeneous systems, you can find the equilibrium in the system by:

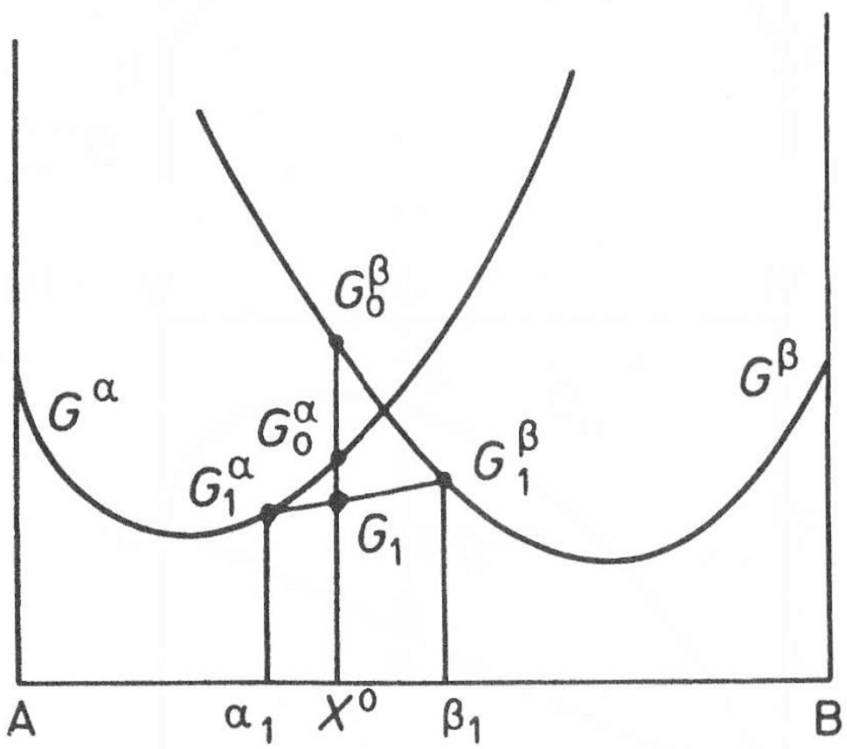
- minimizing the free energy

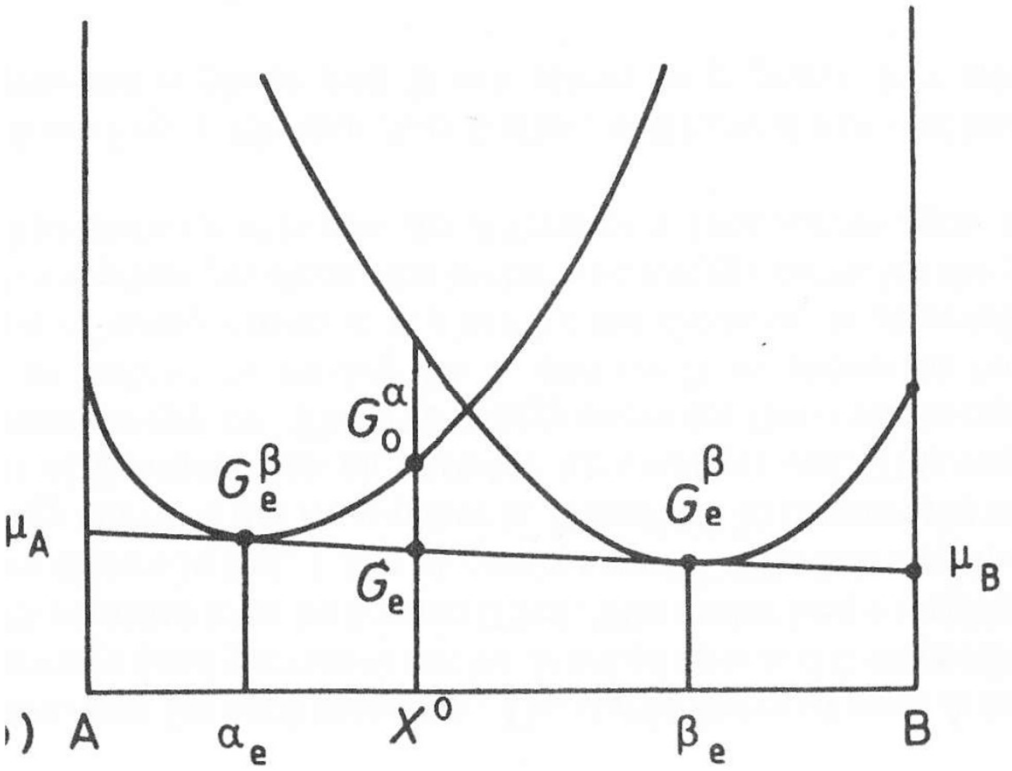
- equating the chemical potentials

- using the common tangent geometrical

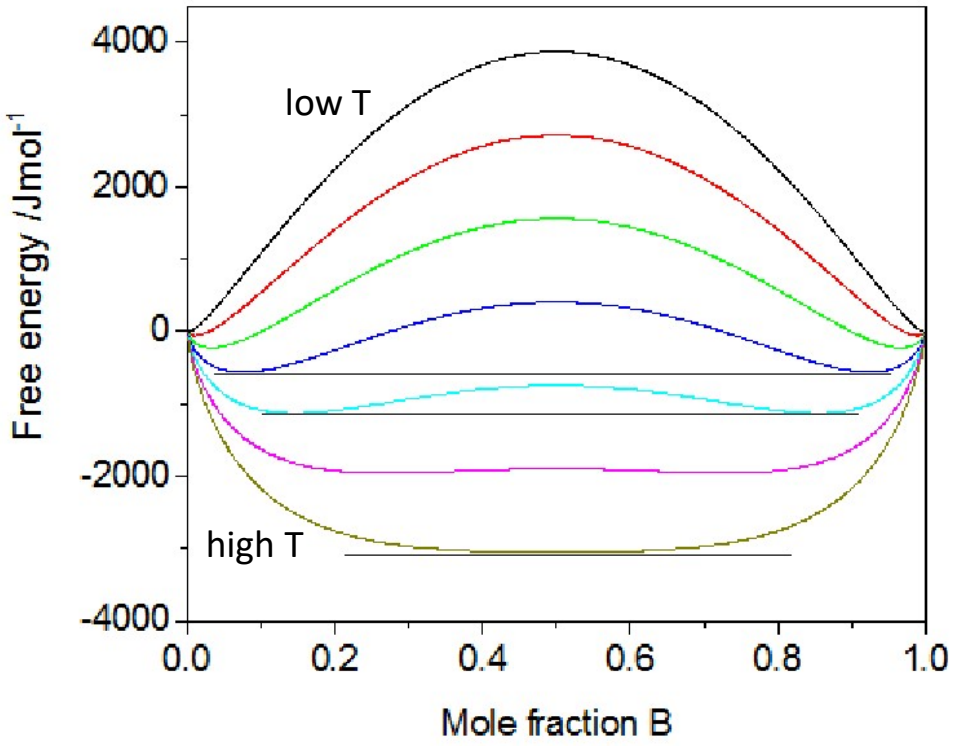
Equilibrium in heterogeneous systems

$$\mu_A^\alpha = \mu_A^\beta \qquad \mu_B^\alpha = \mu_B^\beta$$





Miscibility gaps



The common tangent construction (and chemical potentials) can also be used in a homogeneous system with miscibility gaps.

From thermodynamics to phase diagrams
An example

Free energies computed for **a hypothetical binary A-B system**. In the system there is only *one solid phase,* a ***regular solid solution*** between A and B, and *one liquid phase,* an ***ideal solution*** between A and B.

The relevant properties are:

pure element A $T_m^A = 1200$ K and $\Delta H_m^A = 14$ kJmol^{-1};

pure element B $T_m^B = 1000$ K and $\Delta H_m^B = 12$ kJmol^{-1}

regular solution for solid (crystal) phase $\Omega = 30$ *kJmol*$^{-1}$

T_m^A , T_m^B are the melting points of elements A and B, respectively

ΔH_m^A, ΔH_m^B are the melting enthalpies of elements A and B, respectively

Also remember that at Tm $G_{liquid}=G_{solid}$ and by definition G=H-TS (and also $\Delta G = \Delta H - T\Delta S$)

From thermodynamics to phase diagrams
An example

It is convenient here to chose the free energy of the solid pure elements A and B as reference state at any temperature. So $\boldsymbol{G^A_{solid} = 0}$ **and** $\boldsymbol{G^B_{solid} = 0}$ **at any temperature**.

Then we need to determine the free energies of liquid pure elements A and B. Here we do it for A:

$\Delta G^A_m(T_m = 1200K) = \quad 0$ because at T_m, $G_{solid}=G_{liquid}$

$\Delta G^A_m(T_m = 1200K) = \Delta H^A_m - T_m \Delta S^A_m = 0$

$\Delta H^A_m = \quad 14000$

$$\Delta S^A_m = \frac{\Delta H^A_m}{T_m} = \frac{14000}{1200} \approx 11.67 \frac{J}{mol\ K}$$

$\Delta G^A_{liquid-soli} = G^A_{liquid} - G^A_{solid} = G^A_{liquid}$ and $\Delta G^A_{liquid-solid} = \Delta H^A_{liquid-solid} - T\Delta S^A_{liquid-solid}$

$$G^A_{liquid} = 14000 - 11.67T$$

Similarly for B we get: $G^B_{liquid} = 12000 - 12T$

From thermodynamics to phase diagrams
An example

The free energy of the regular solid solution A, B will then be:

$$G_{solid}^{A,B} = X_A G_{solid}^{A} + X_B G_{solid}^{B} + R\mathrm{T}(X_A lnX_A + X_B lnX_B) + \Omega X_A\, X_B =$$

$$8.31\ \mathrm{T}(X_A lnX_A + X_B lnX_B) + 30000\ X_A\, X_B$$

The free energy of the ideal liquid solution A, B will then be:

$$G_{liquid}^{A,B} = X_A G_{liquid}^{A} + X_B G_{liqui}^{B} + R\mathrm{T}(X_A lnX_A + X_B lnX_B) =$$

$$(14000 - 1.17T)X_A + (12000 - 1.2T)X_A + 8.31\ \mathrm{T}(X_A lnX_A + X_B lnX_B)$$

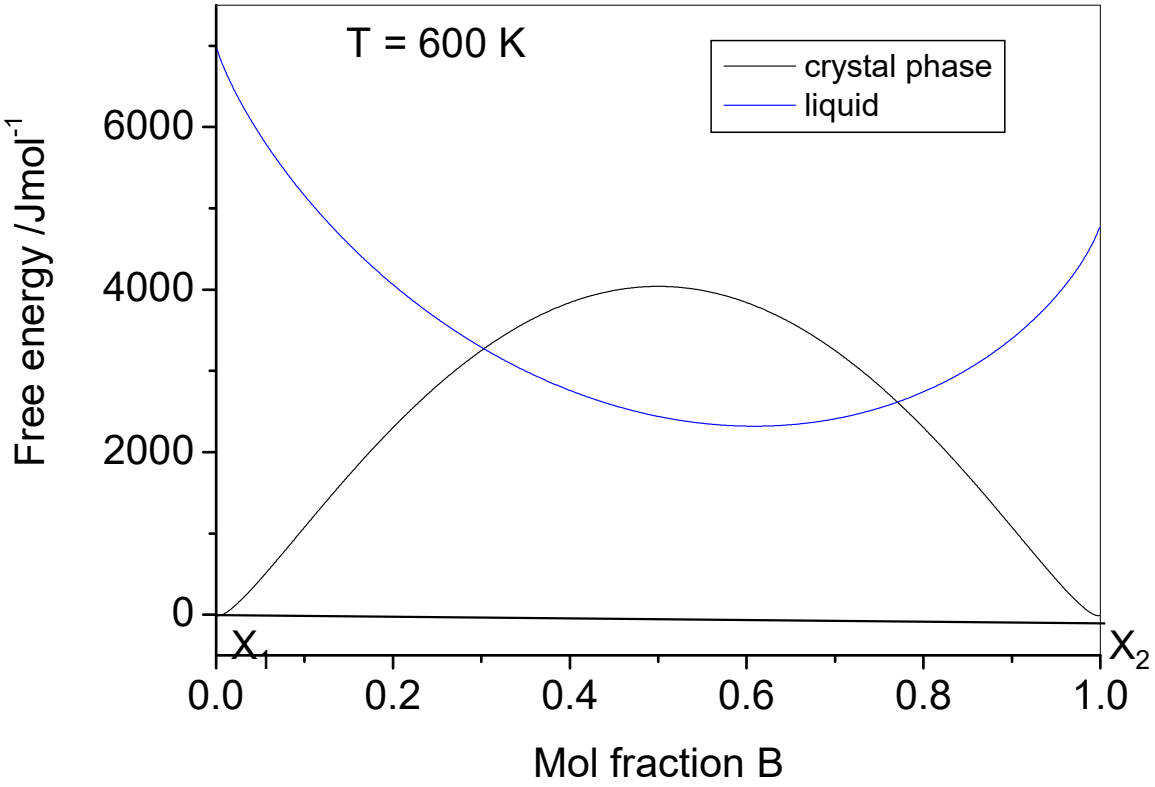
We can compute now the free energy curves at different constant temperatures as a function of X_B…

Thermodynamics and phase diagrams

At low T (600 K), we have a miscibility gap in the solid phase.

In equilibrium, two solid solutions with different compositions (X_1 and X_2) are stable (common tangent construction).

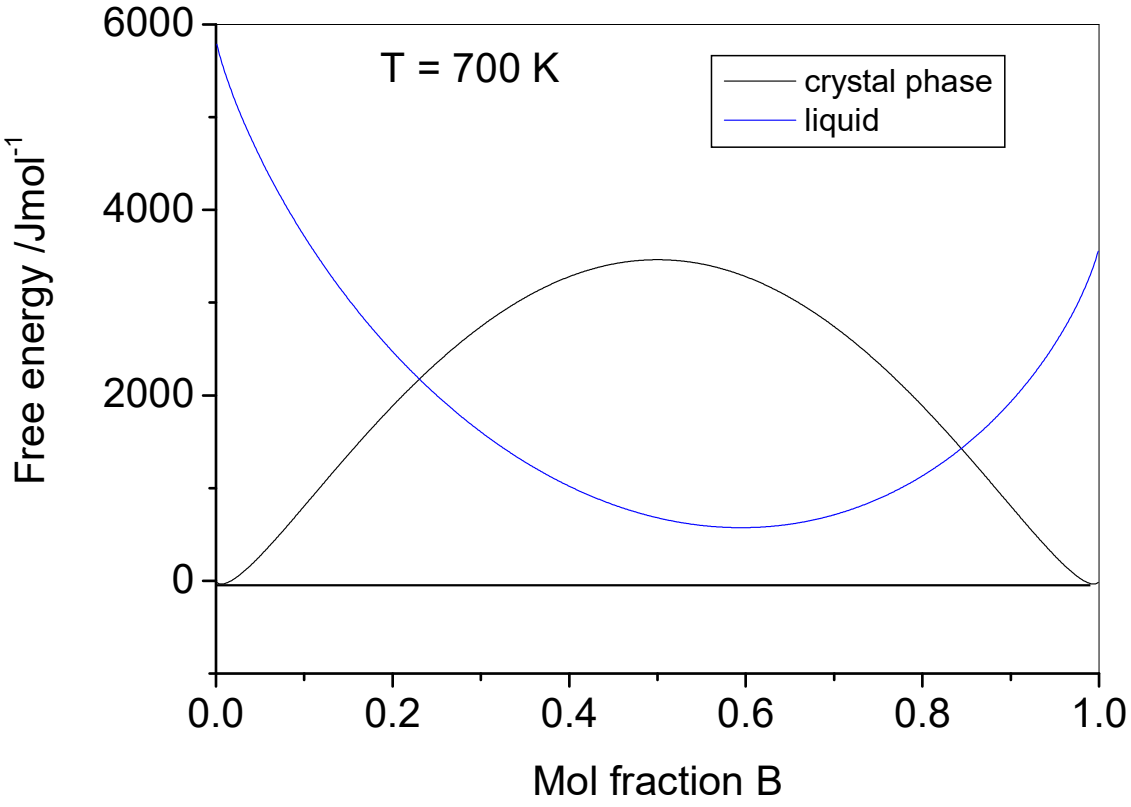
X_1 and X_2 are the molar fractions at tangent points.



Thermodynamics and phase diagrams

At a slightly higher T (700 K), the free energy of the liquid phase decrease and gets close to that of the solid one.

In equilibrium, the are still two solid solutions with different compositions are stable (common tangent construction).



Thermodynamics and phase diagrams

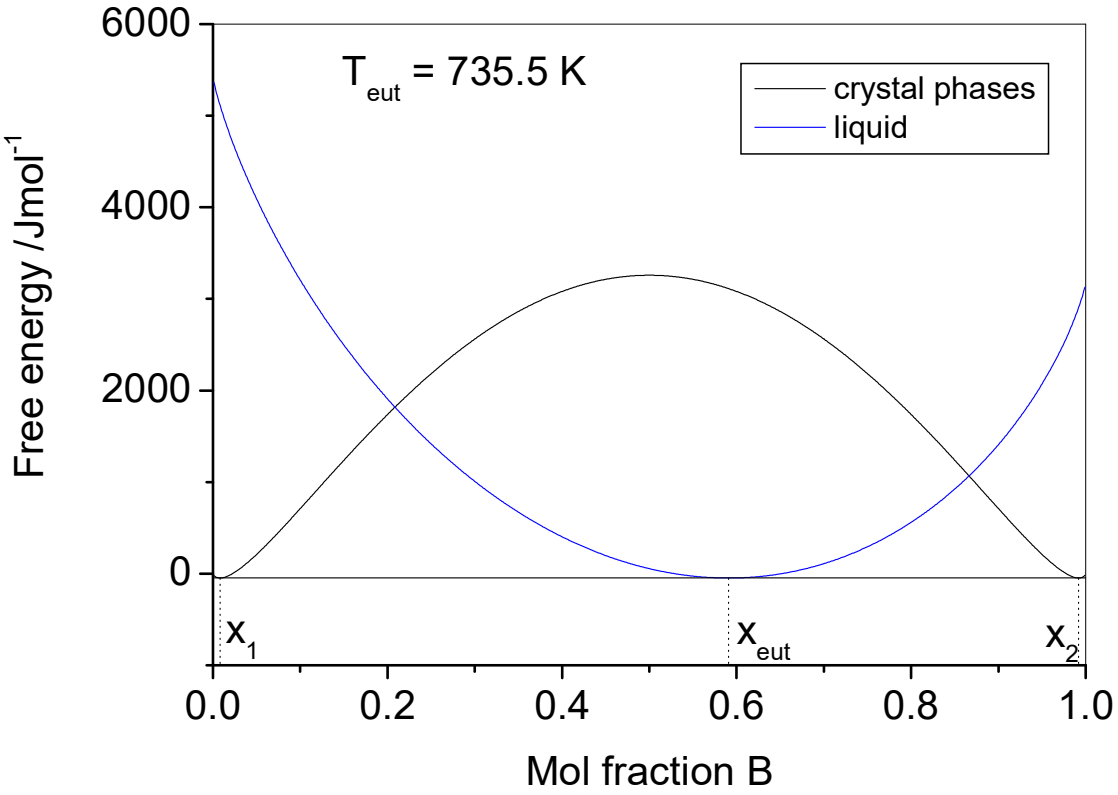
At T=735.5 K, three phases are in equilibrium according to the common tangent construction: the liquid phase (composition X_{eut}) and two solid solutions with different compositions (X_1 and X_2).

Invariant three phase equilibrium (eutectic)

liquid ←→ $\alpha_1 + \alpha_2$

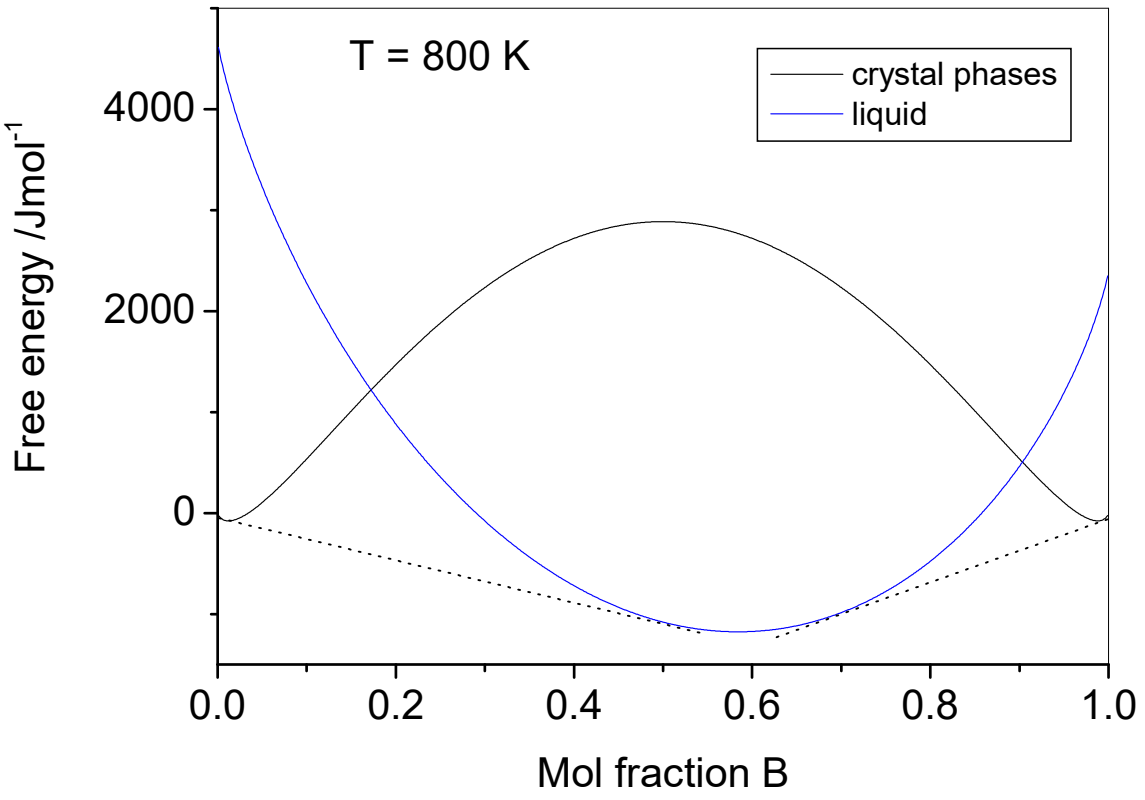
Gibbs phase rule

$v = c - f + 1 = 0$



Thermodynamics and phase diagrams

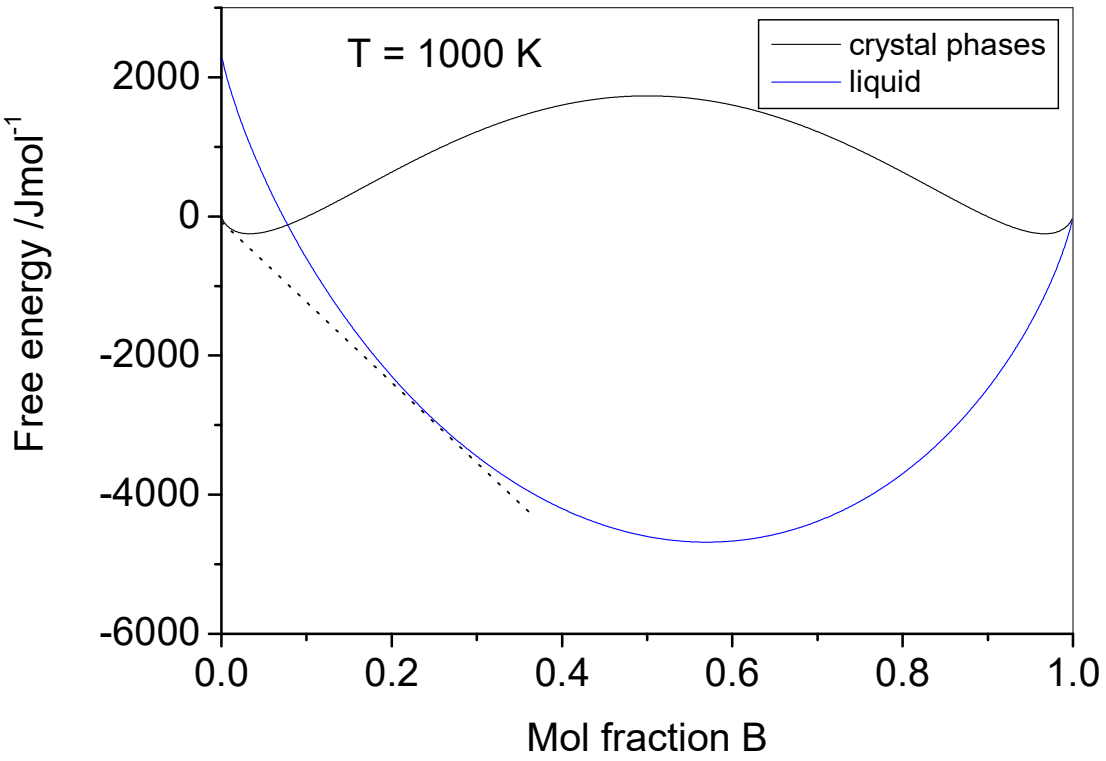
Three single-phase fields; two two-phase fields; two common tangents.



Thermodynamics and phase diagrams

Melting point of B (T=1000 K)

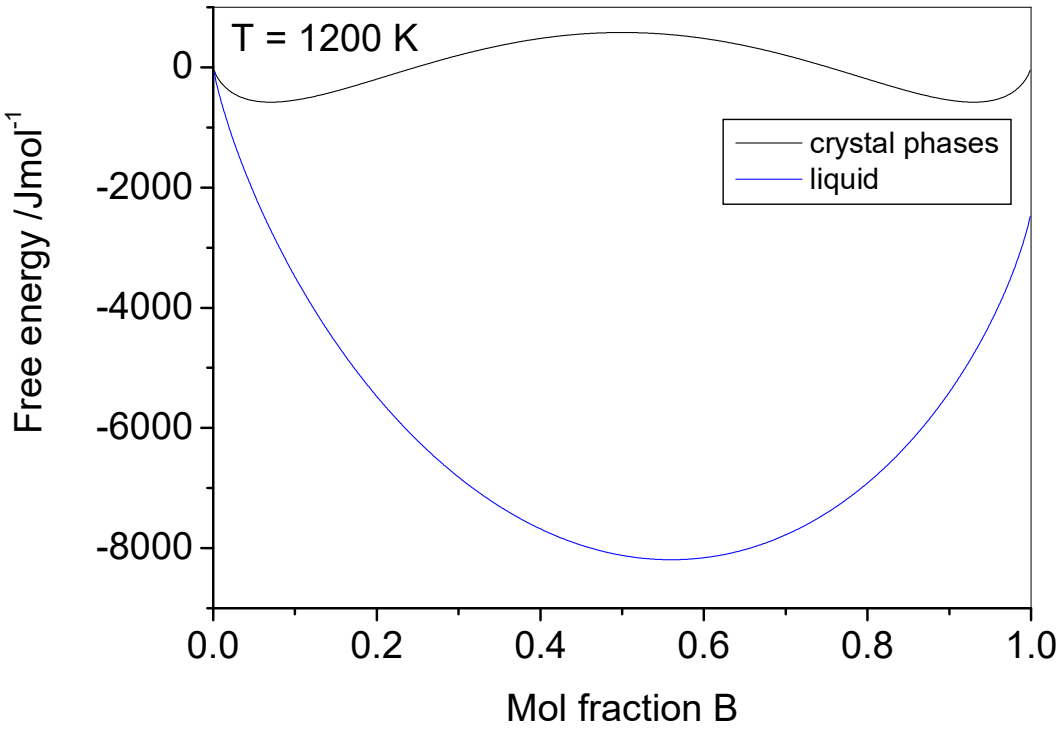
Two single-phase fields; one two-phase fields; one common tangent in the A-rich part.



Thermodynamics and phase diagrams

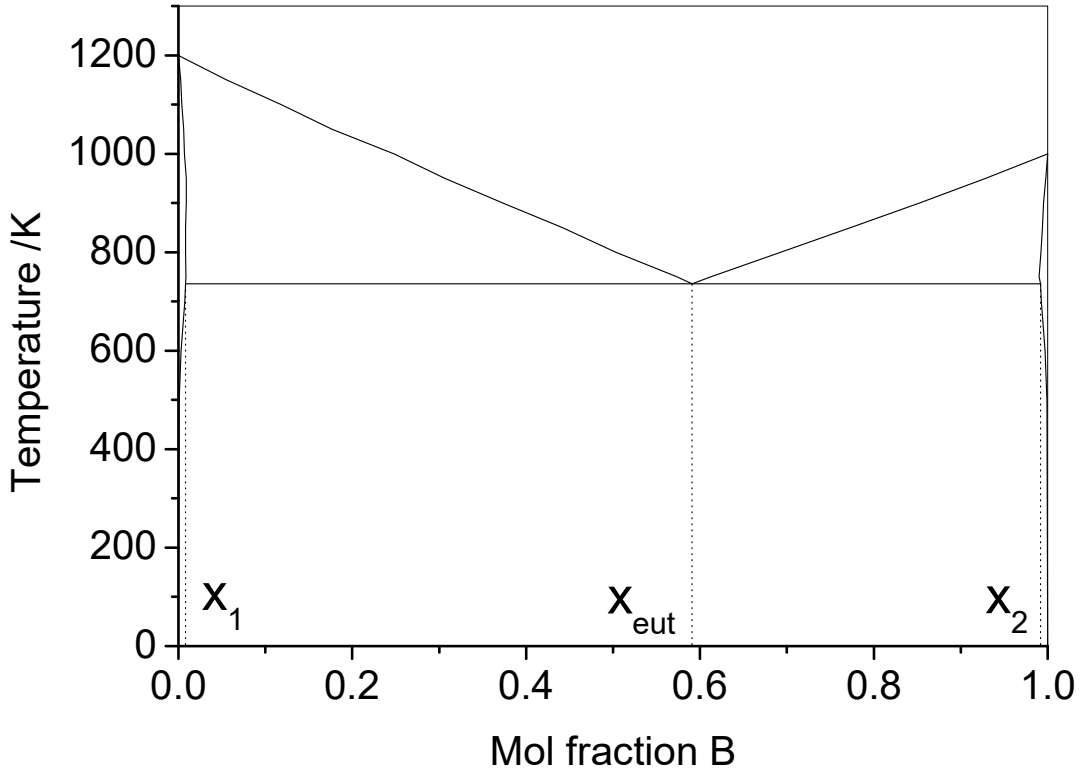
Melting point of A

One-phase field, the liquid is stable at any composition



Thermodynamics and phase diagrams

The resulting phase diagram is:



Compounds

The free energy of formation of compounds from their constituents is

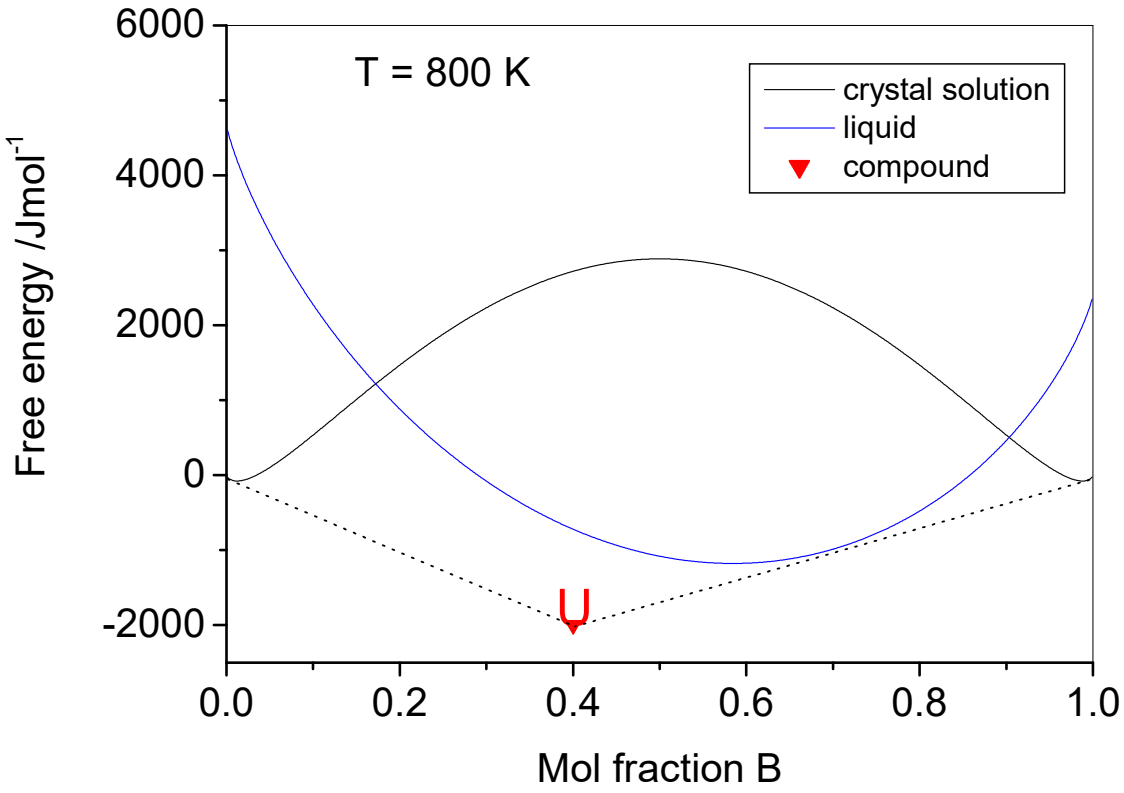
$\Delta G_{for} = \Delta H_{for} - T\Delta S_{for}$.

ΔH_{for} usually negative

ΔS_{for} small, nil, even negative

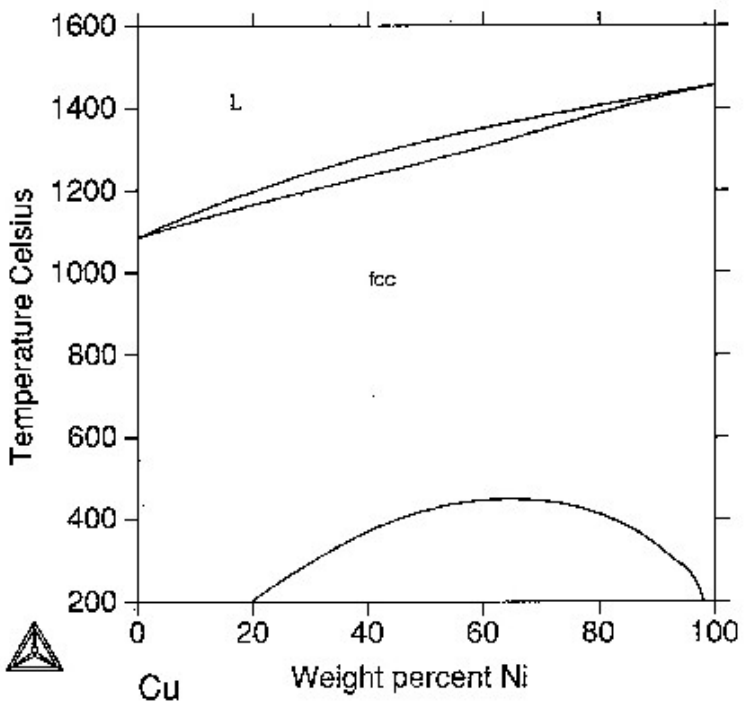
U-shaped free energy function centered at stoichiometry.

Compound free energy added to previous scheme

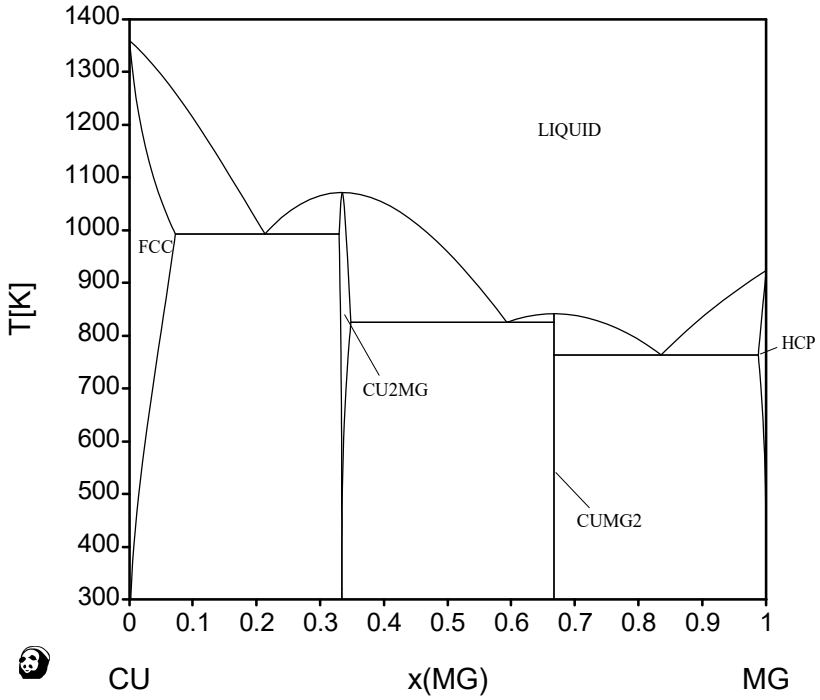


Other binary examples

Cu-Ni: full miscibility in liquid and crystal phases + low temperature gap.

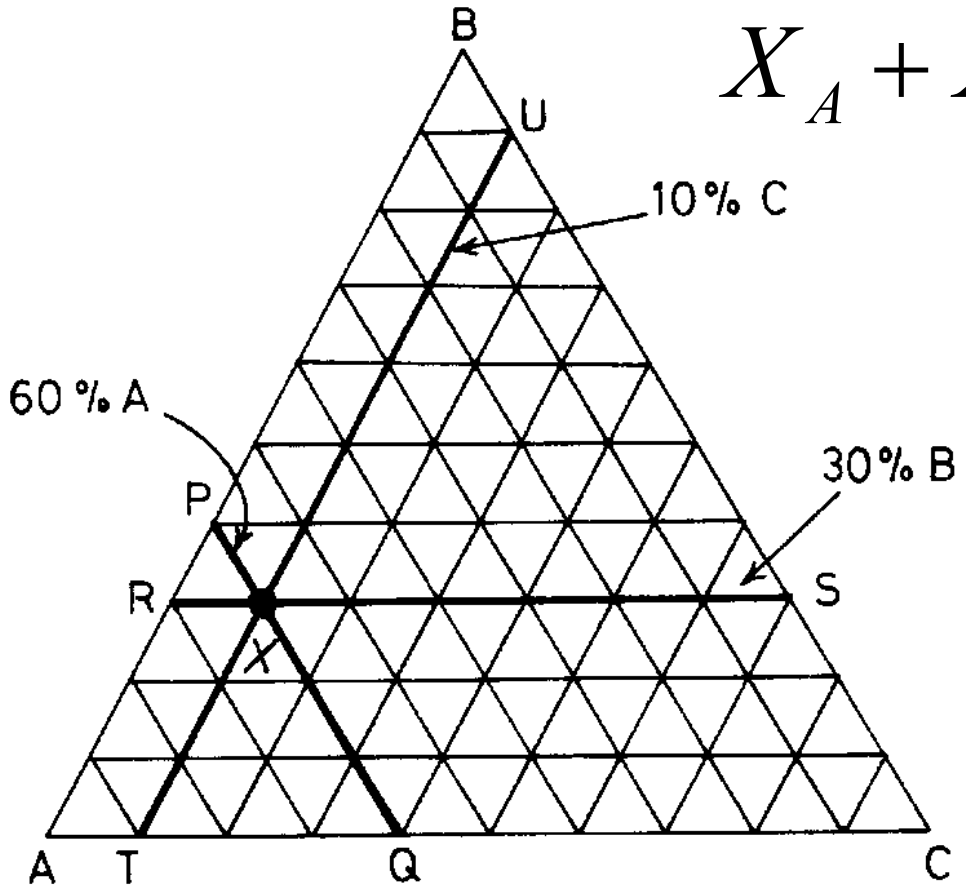


Cu-Mg:
$CuMg_2$ = stoichiometric compound,
Cu_2Mg = deviation from stoichiometry



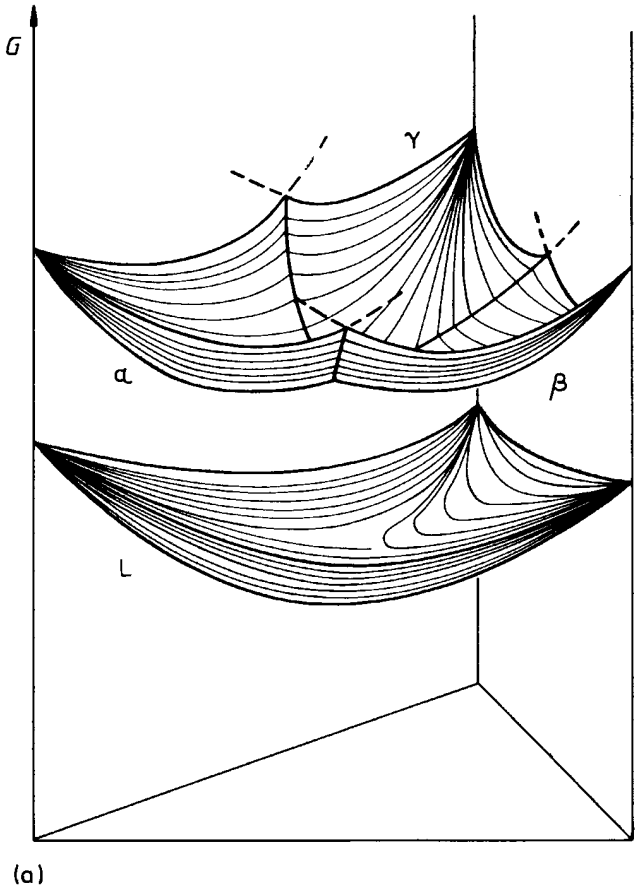
Ternary phase diagrams

$$X_A + X_B + X_C = 1$$

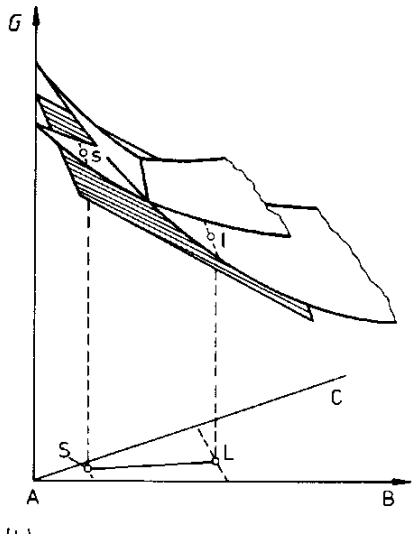


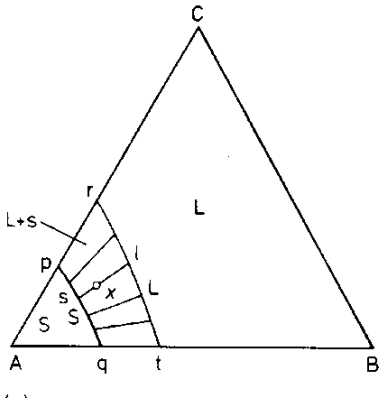
The Gibbs triangle

Ternary phase diagrams



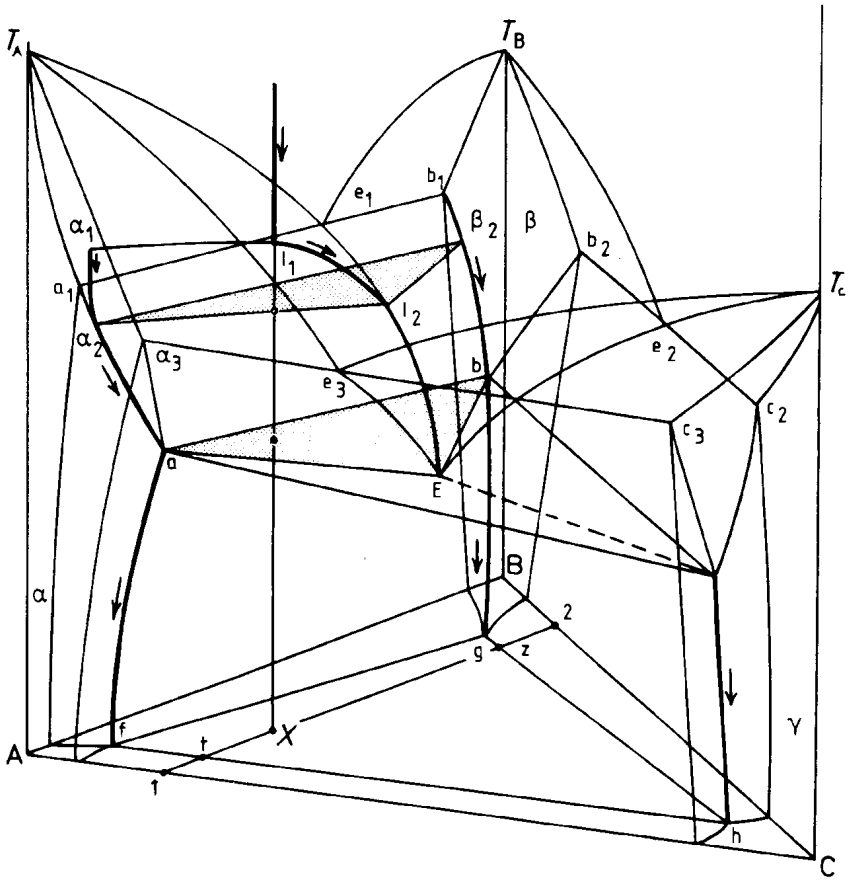
(a)

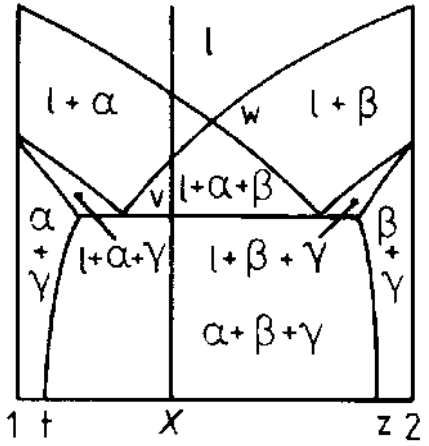




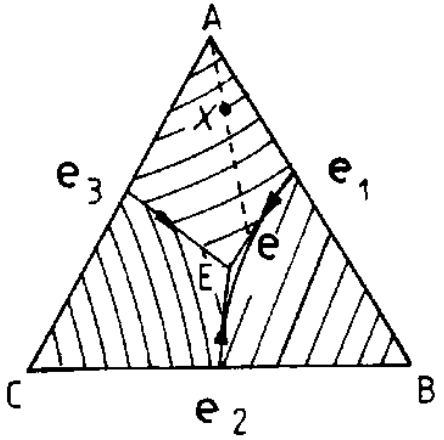
Tangential plane and construction of tie-lines.

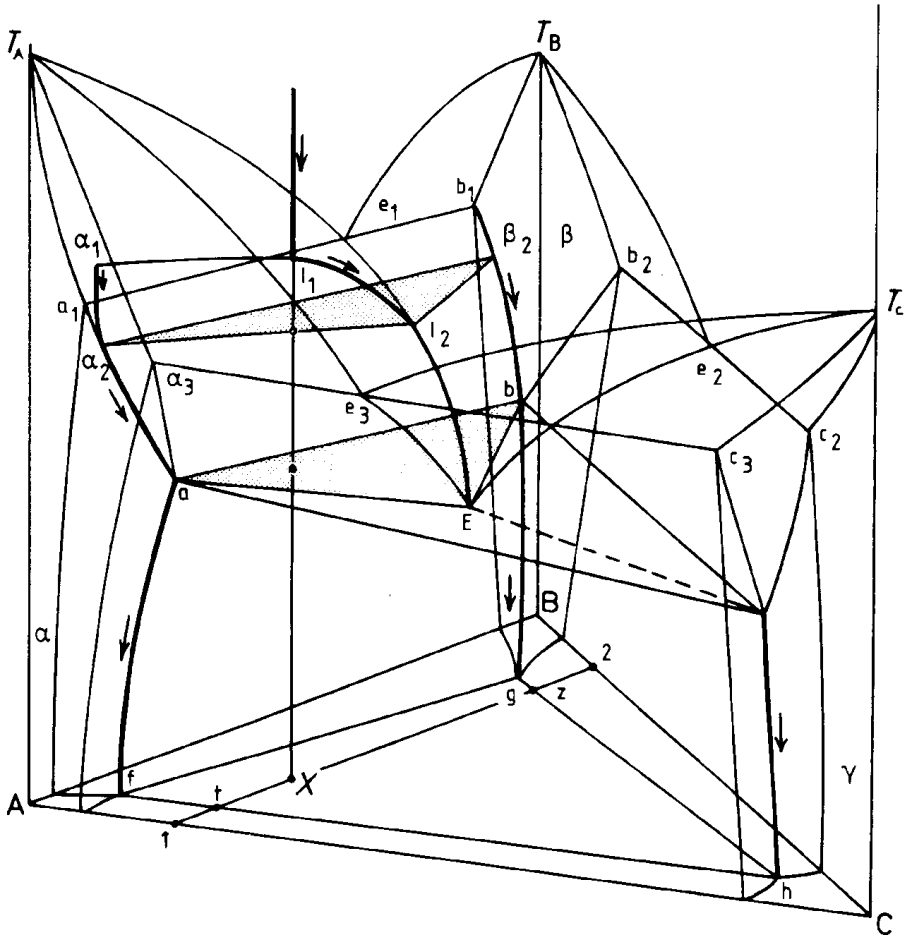
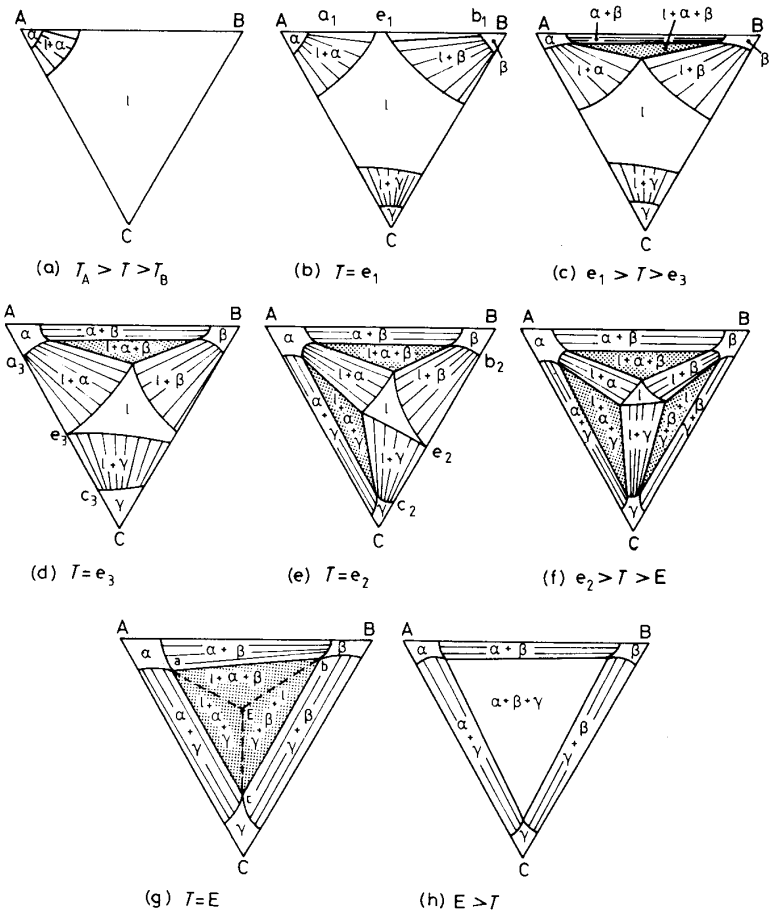
Ternary phase diagrams: pseudobinaries and liquidus projetions





Pseudobinary



Liquidus projection

Ternary phase diagrams: isothermal sections