METRO
MEtallurgical TRaining On-line

Thermodynamic basis of modeling of phase change phenomena

Robert Dyja
CzUT

Education and Culture

Plan of presentation

- Basic concepts
- Gibbs free energy
- Lever rule
- Cooling curves
- Binary phase equilibrium diagrams
- Ternary phase equilibrium diagrams

Basic concepts

- Alloy
- Phase
- System
- Phase equilibrium
- Thermodynamic equilibrium

Basic concepts

- Helmholtz free energy

$$F = E - TS$$

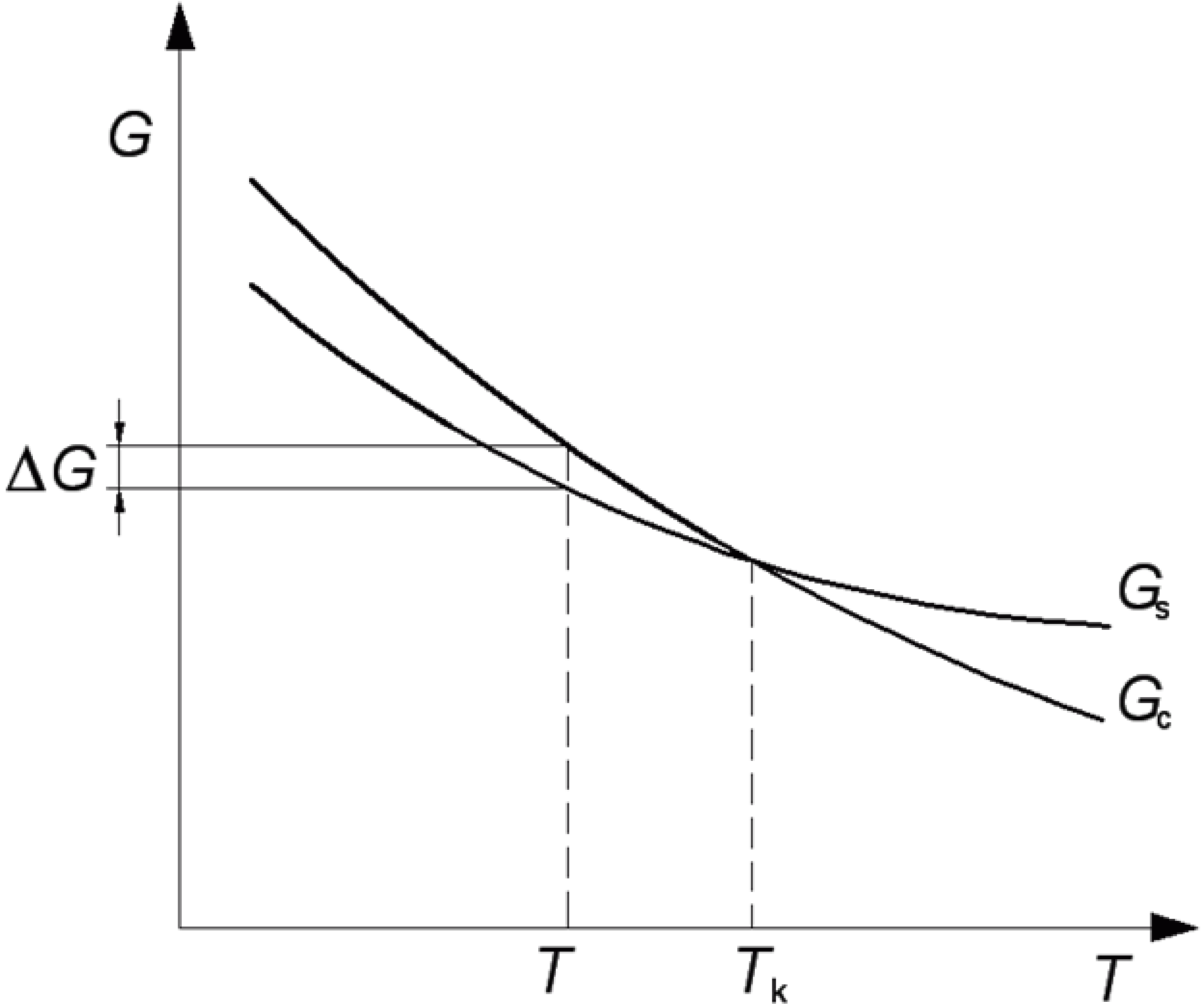
E – internal energy, *T* - temperature, *S* - entropy

- Gibbs free energy

$$G = E + pV - TS$$

p - pressure, *V* - volume

Gibbs free energy



Gibbs phase rule

Equation describing Gibbs phase rule:

$$S = n - c - f + p$$

S – number of degrees of freedom

n – number of dependent components

c - number of reversible chemical reactions

f – number of phases

p – number of physical factors affecting equilibrium

Gibbs phase rule

If there is no chemical or other reversible reactions between components and only physical factor which influences system is temperature, then phase rule is simplified to this equation:

$$S = n - f + 1$$

S – number of degrees of freedom

n – number of dependent components

f – number of phases

Newton law

Cooling is described by Newton law

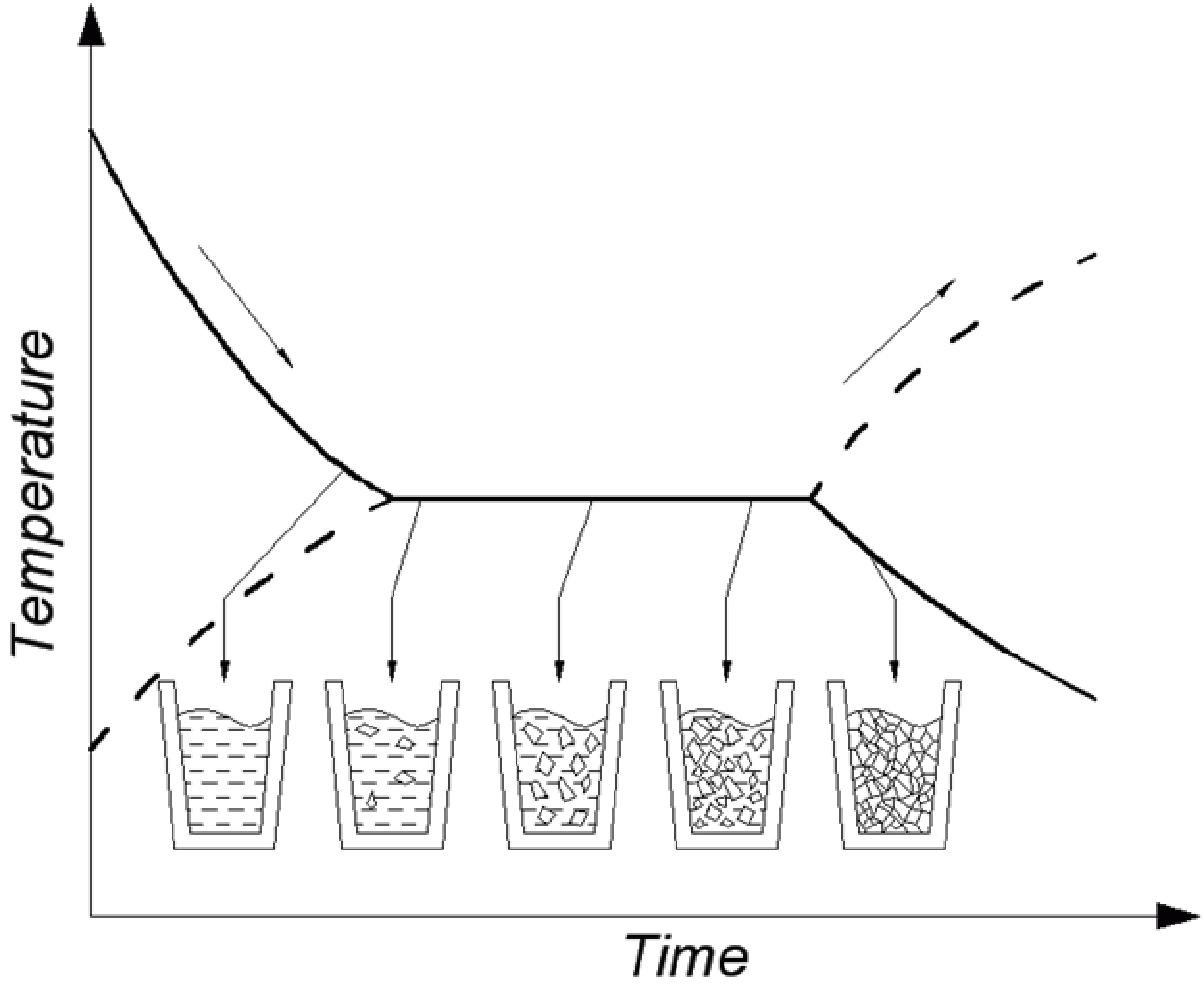
$$\Delta T = \Delta T_0 \cdot e^{-\alpha\tau}$$

ΔT_0 — initial difference between temperature of heated body and surrounding environment (for time $\tau = 0$)

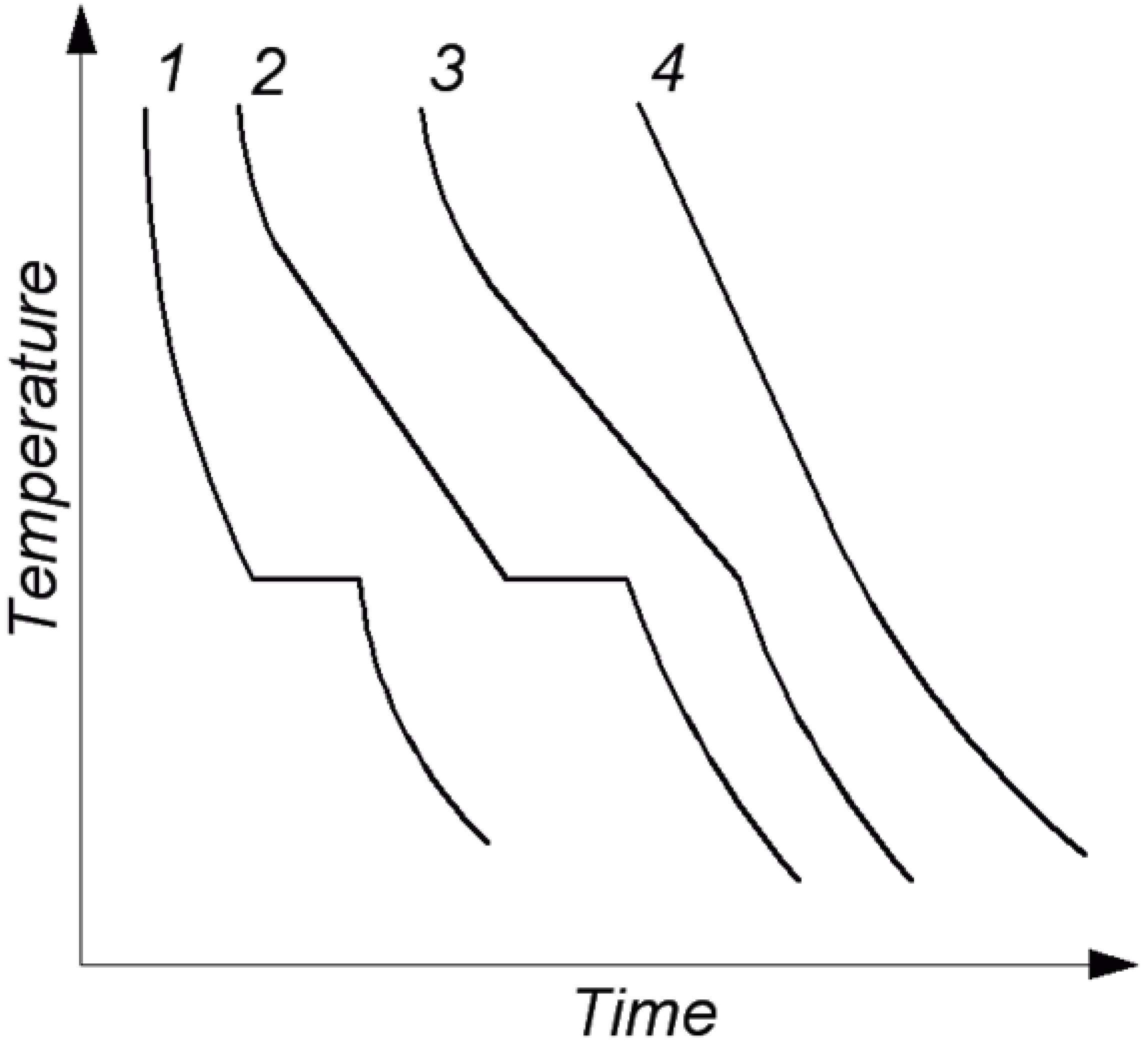
ΔT - denotes difference between temperature of heated body and ambient temperature for time τ

α – cooling factor

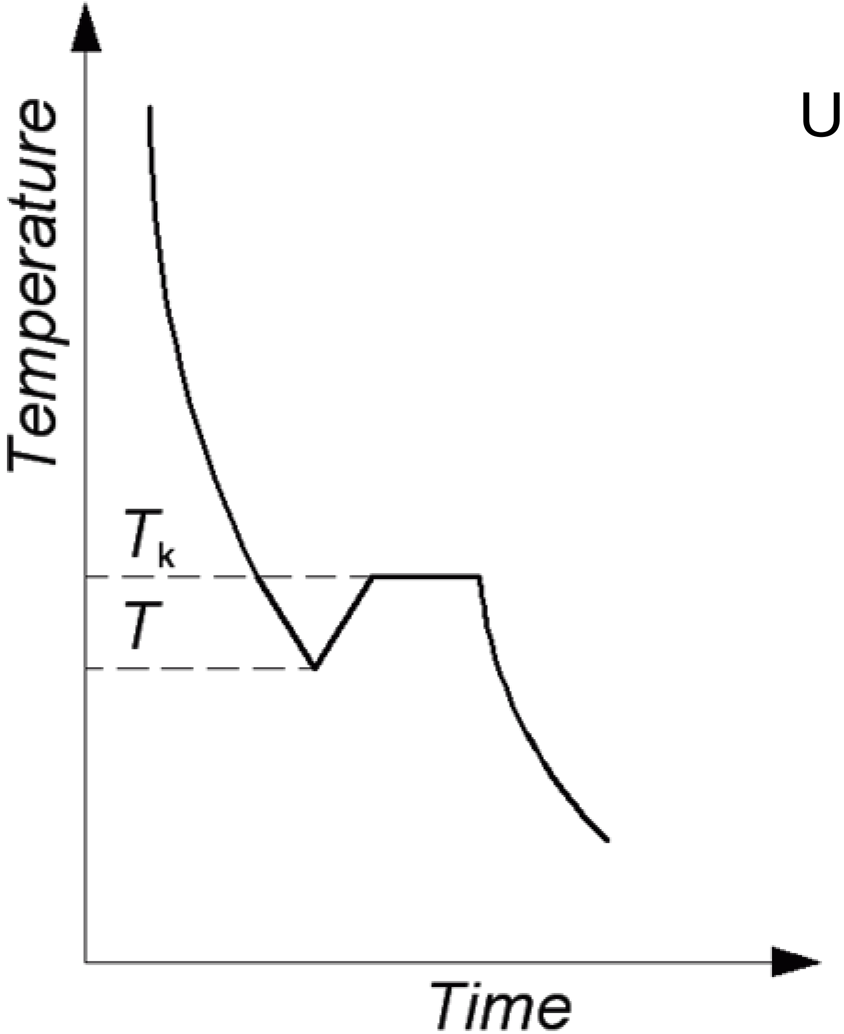
Cooling curves



Cooling curves



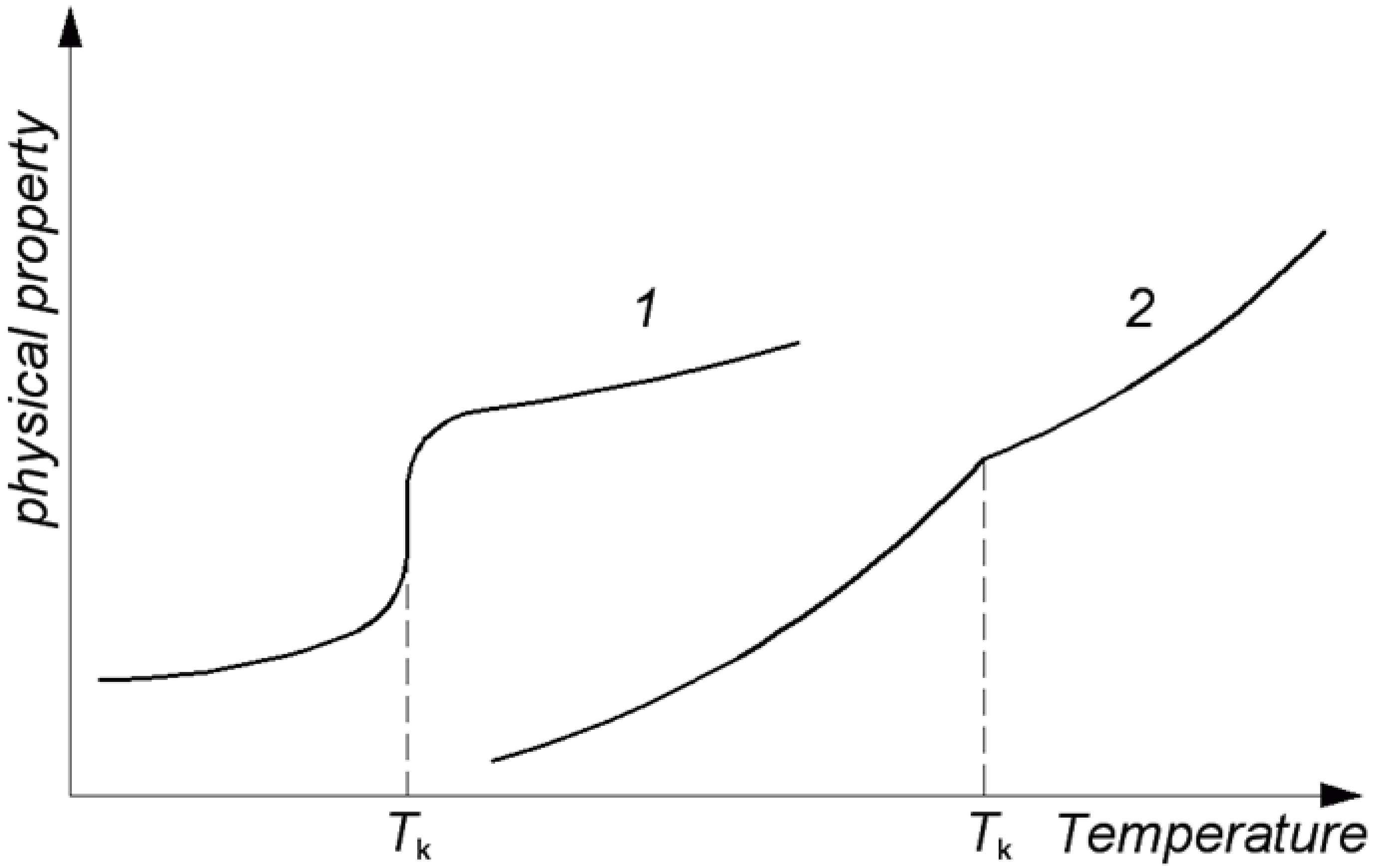
Undercooling



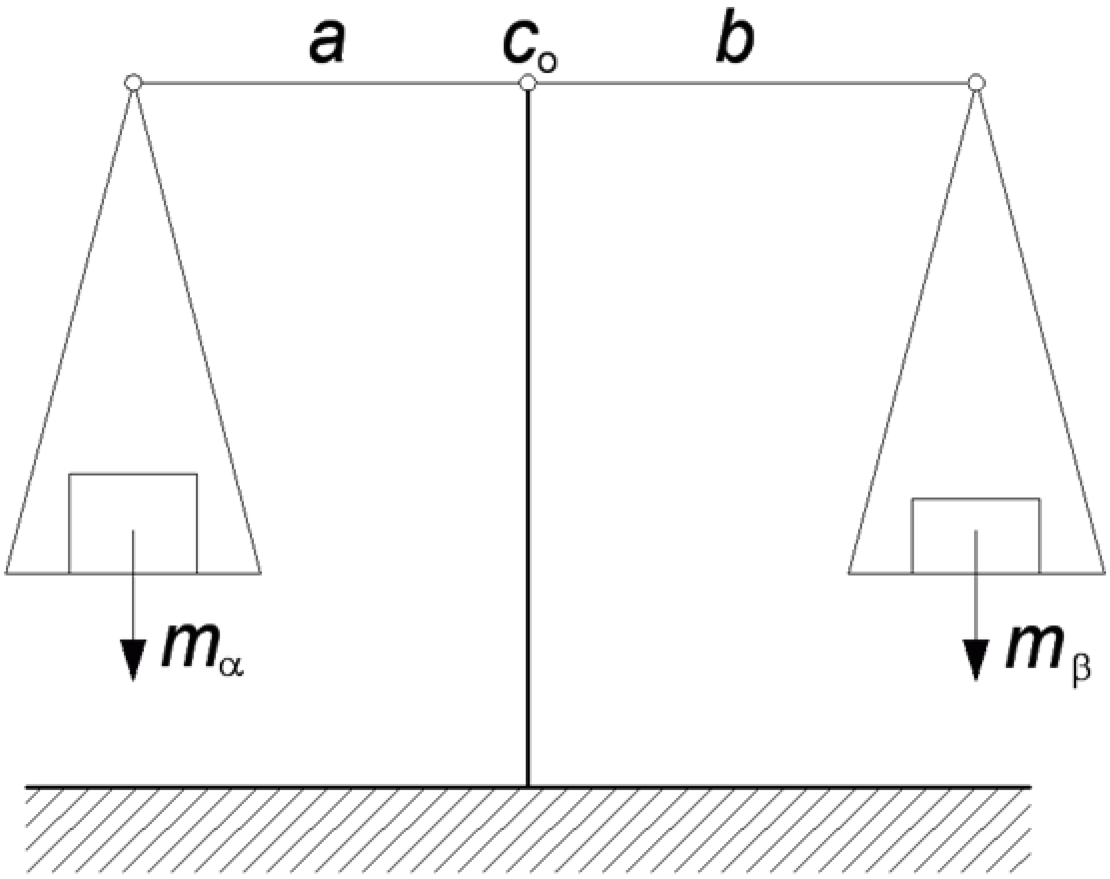
Undercooling:

$$\Delta T = T_K - T$$

Physical properties of cooled materials



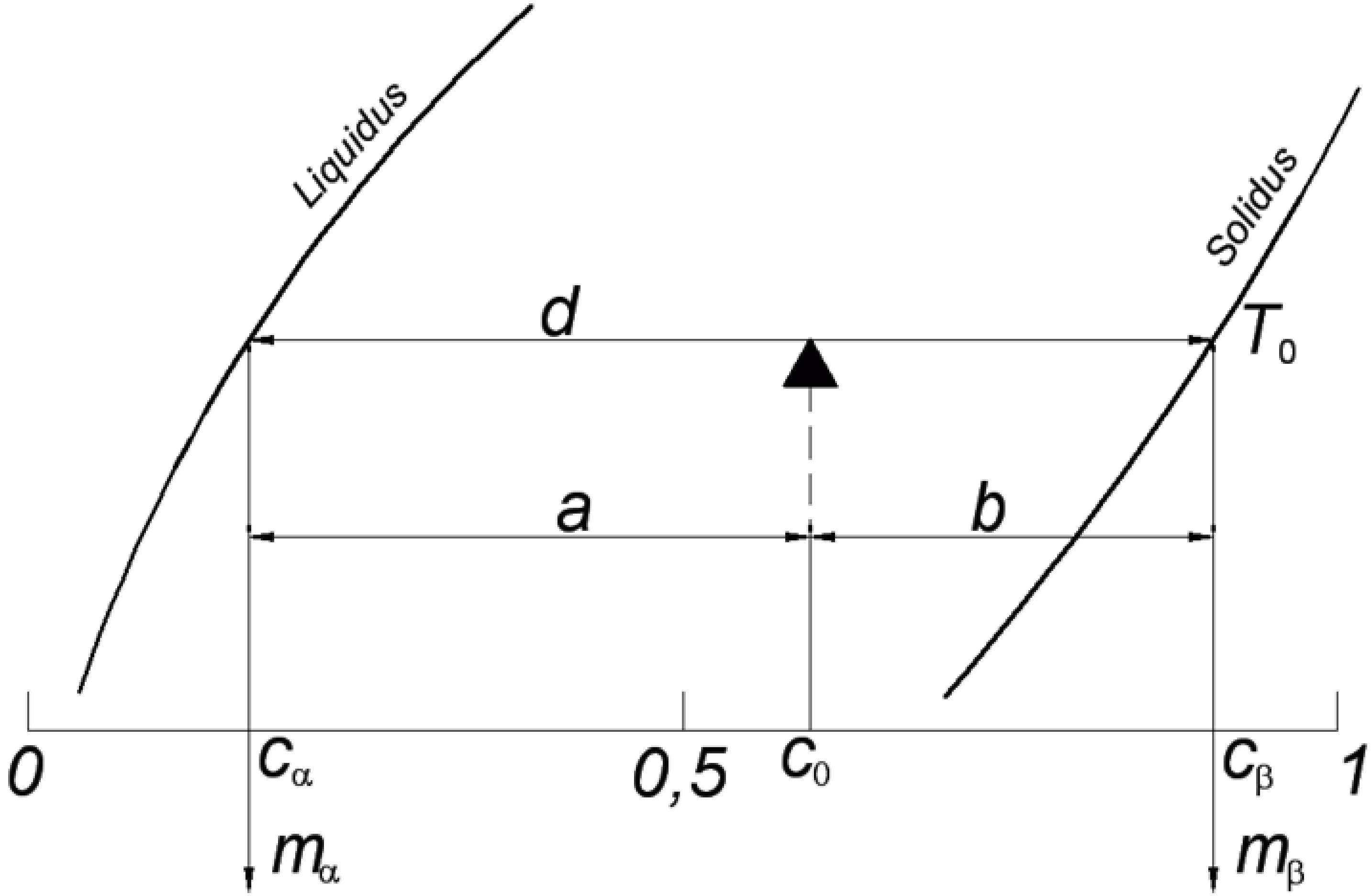
Lever rule



$$m_\alpha a = (1 - m_\alpha) b \quad (1)$$

$$\frac{m_\alpha}{1 - m_\alpha} = \frac{b}{a} \quad (2)$$

Lever rule



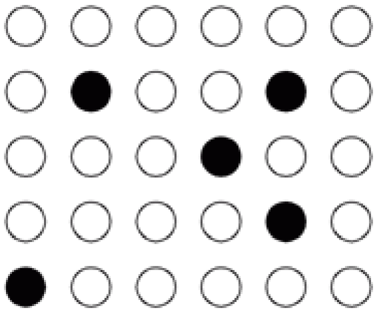
Alloying phases

We can divide phases on

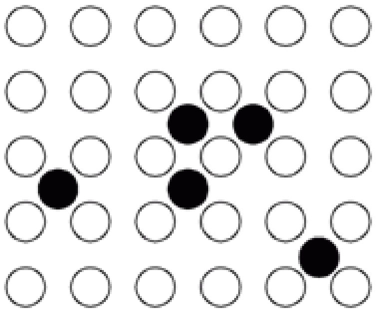
- Chemical elements
- Solid solutions
- Intermetallic phases

Alloying phases

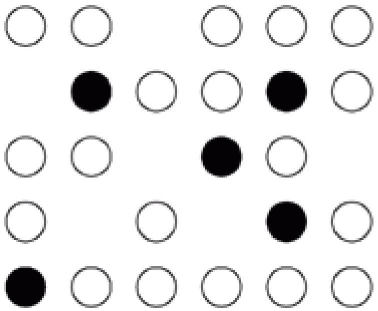
Solid solutions:



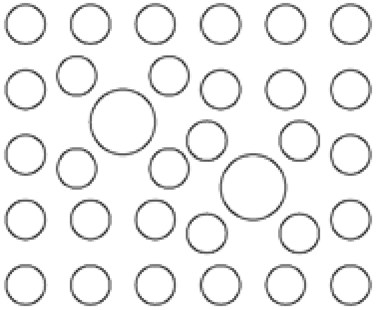
Picture 1



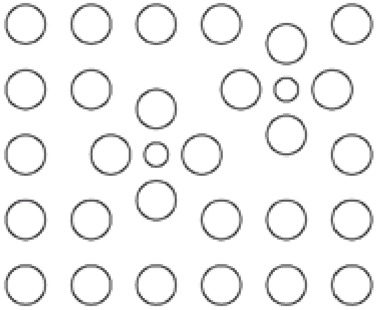
Picture 2



Picture 3



Picture 4



Picture 5

Alloying phases

Intermetallic phases are characterized by:

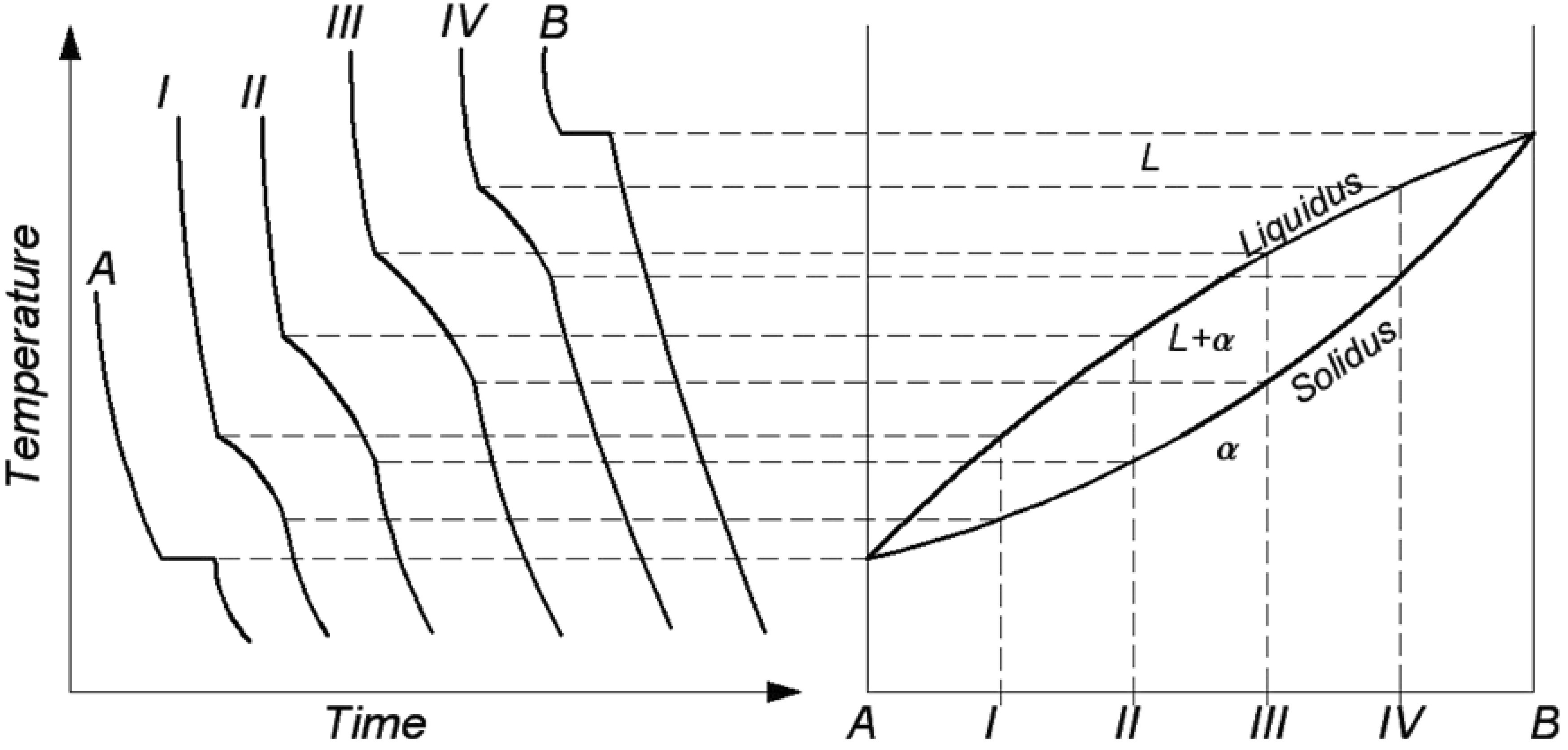
- suitable crystal structure
- filling by atoms of chemical compounds typical for them positions in space lattice
- valence of components mostly runs away from valence in chemical conventional compounds
- the metallic bond

Binary systems

Hume-Rothery conditions:

- Similar type of crystal lattice of components
- Factor of atom size
- The close neighborhood of elements forming the solution in periodical system
- Effect of relative valence

Binary systems – binary isomorphous system



Binary systems – binary isomorphous system

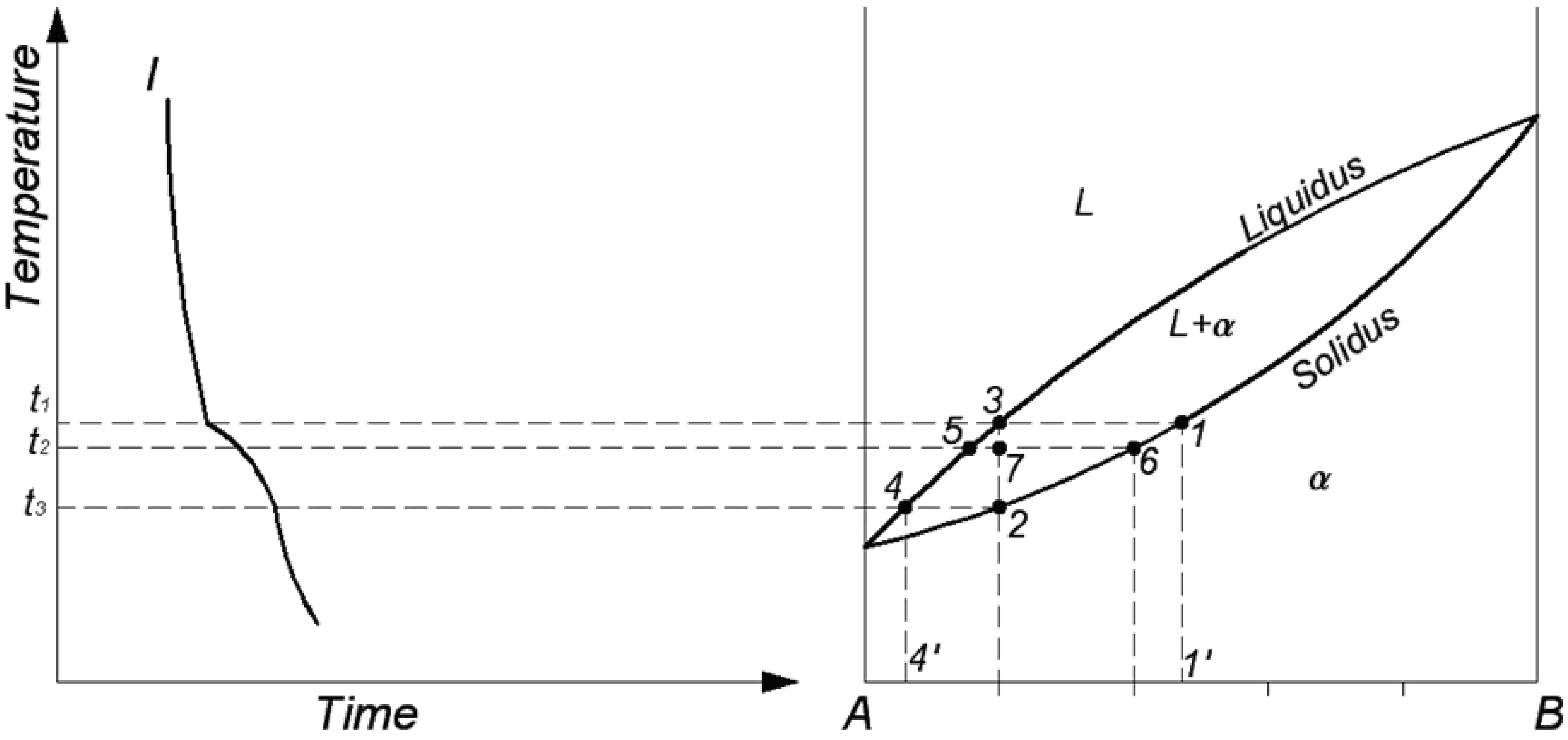
- Gibbs phase rule for region *L* and region α:

$$S = n - f + 1 = 2 - 1 + 1 = 2$$

- Gibbs phase rule for region *L* + α:

$$S = n - f + 1 = 2 - 2 + 1 = 1$$

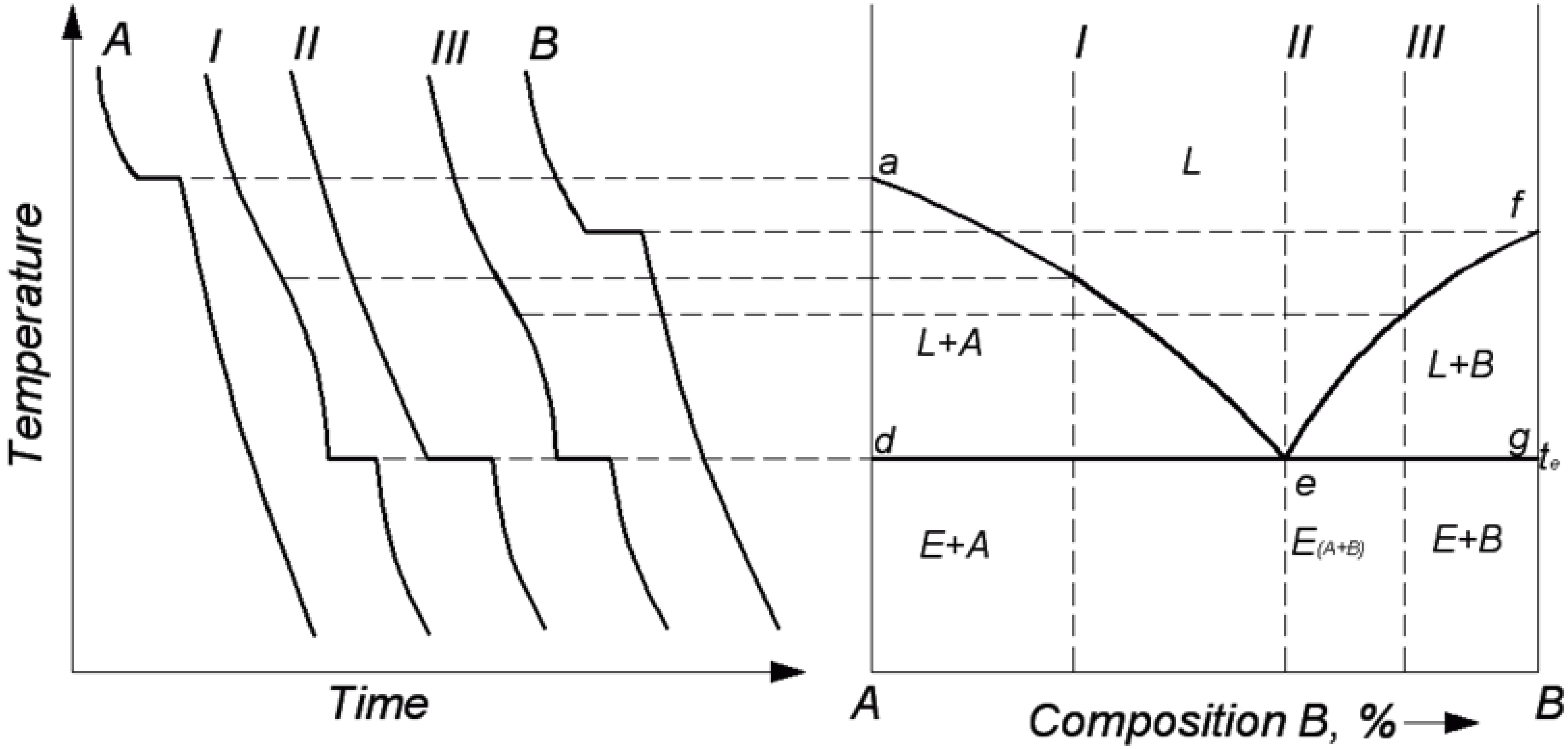
Binary systems – binary isomorphous system



Binary systems

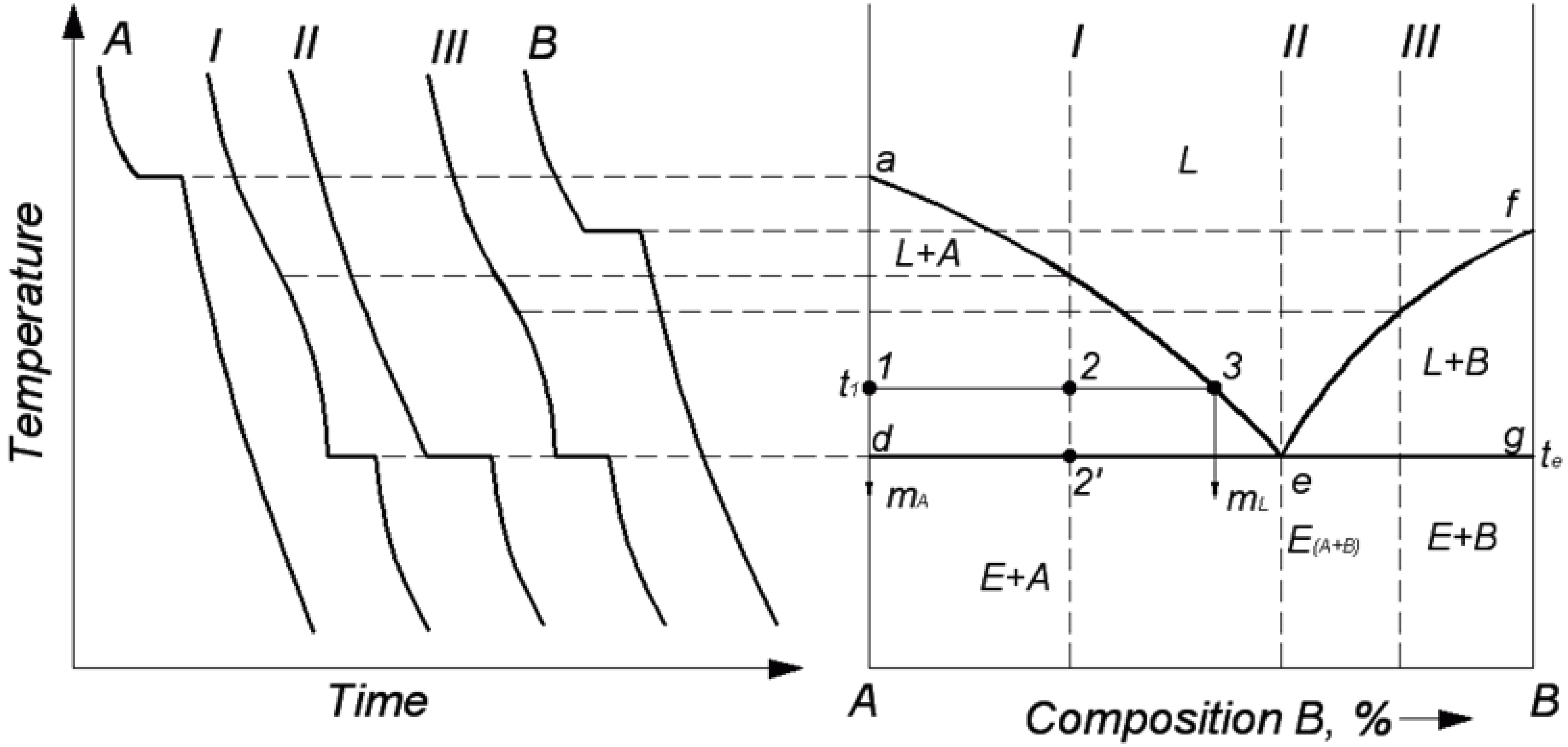
- Systems with no solubility in solid state (system with eutectic transition)
- Eutectic transition is characterized by:
  - It occurs in fixed temperature
  - Composition of liquid from which eutectics is formed is always the same
  - Relation of phases in eutectics is constant

Binary systems with no solid solubility – eutectic system

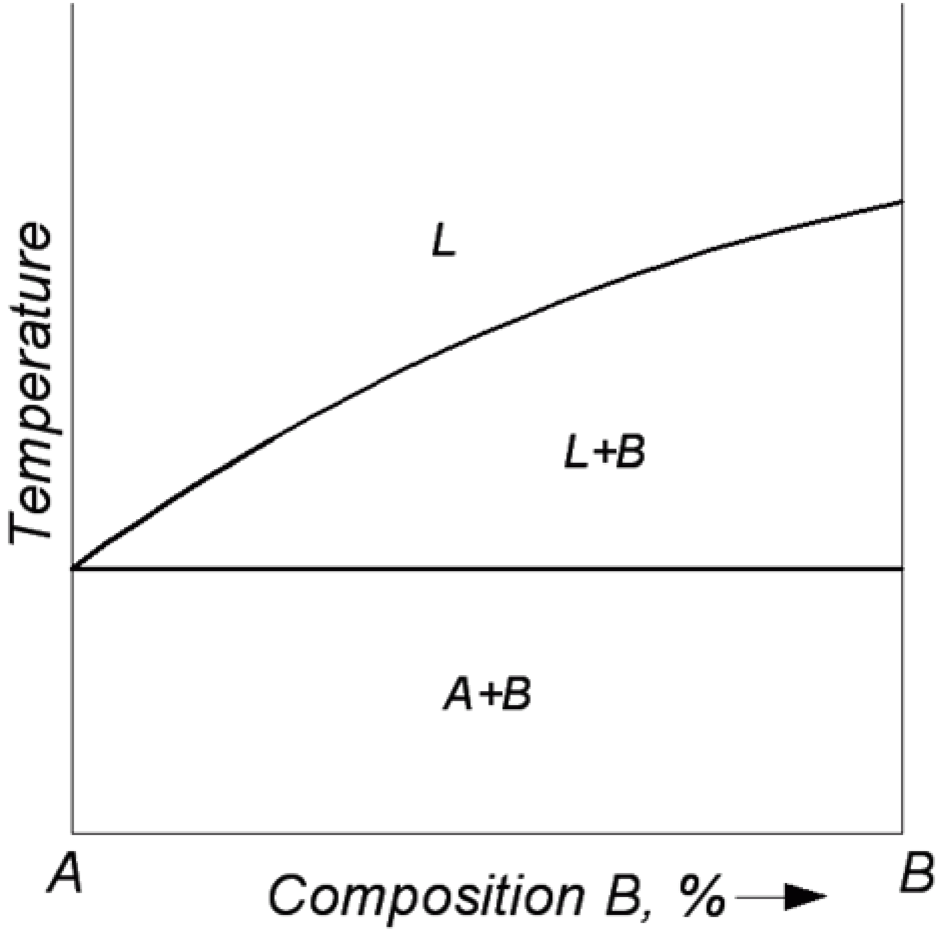


$$L_e \underset{cooling}{\overset{heating}{\rightleftarrows}} A + B$$

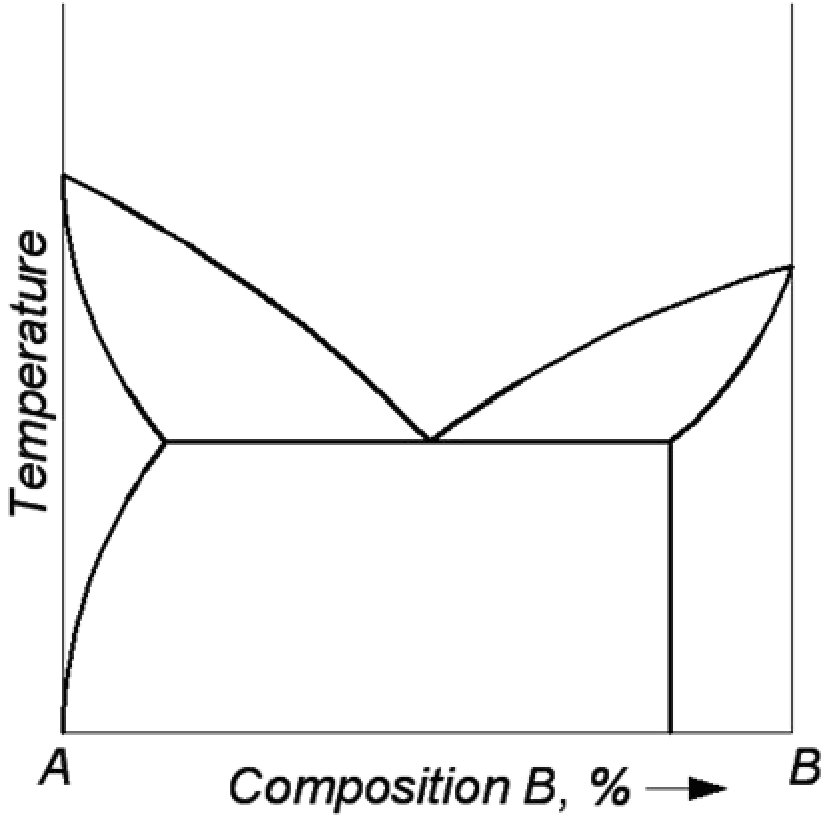
Binary systems with no solid solubility – eutectic system

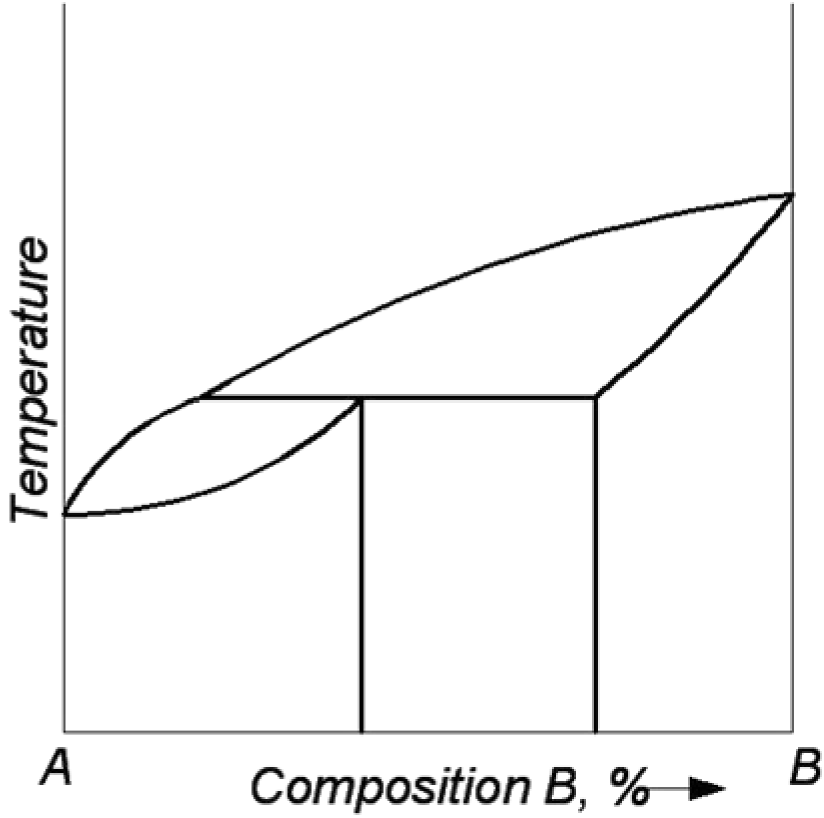


Binary systems with no solid solubility

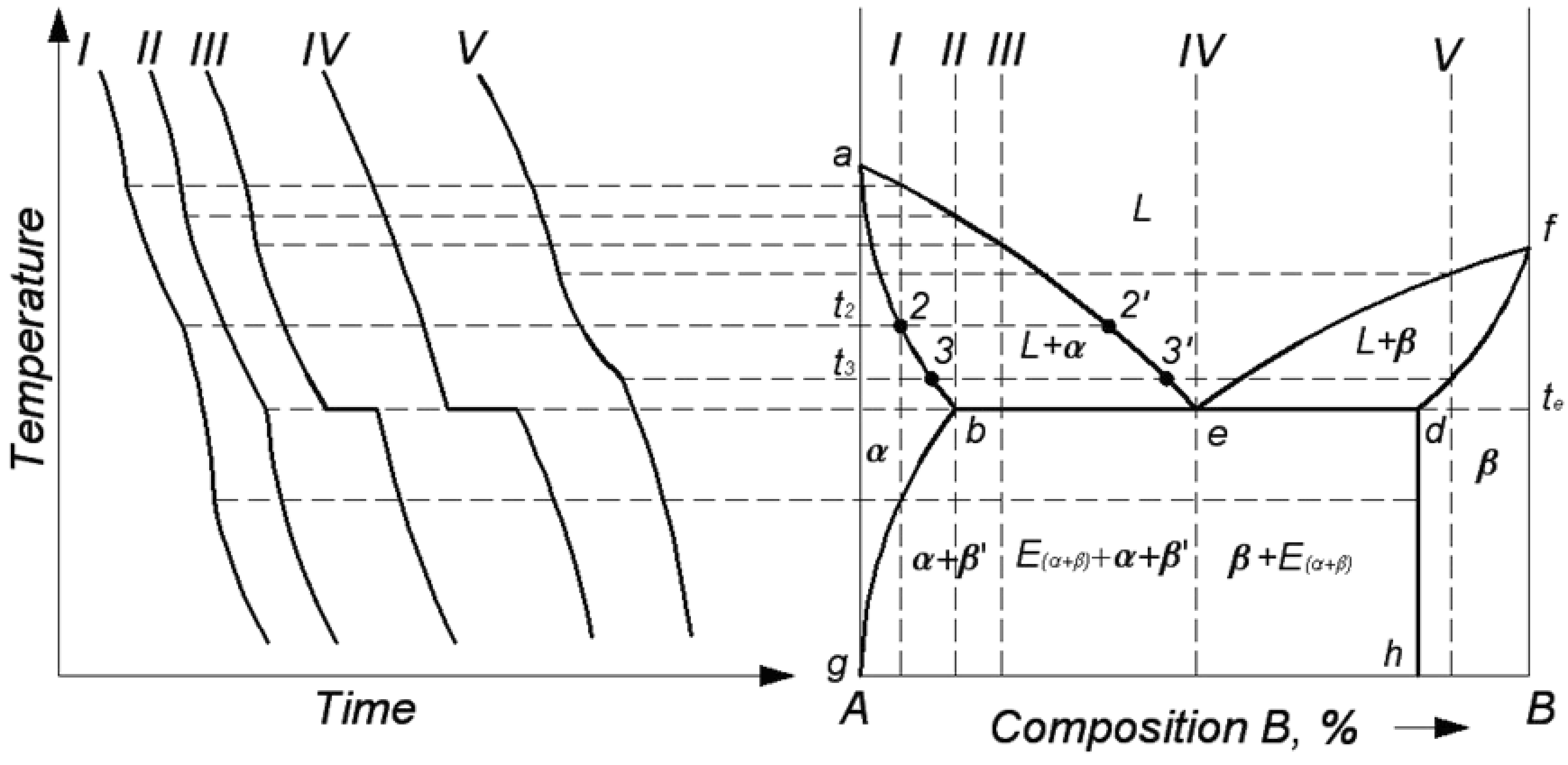


Binary systems with limited solid solubility

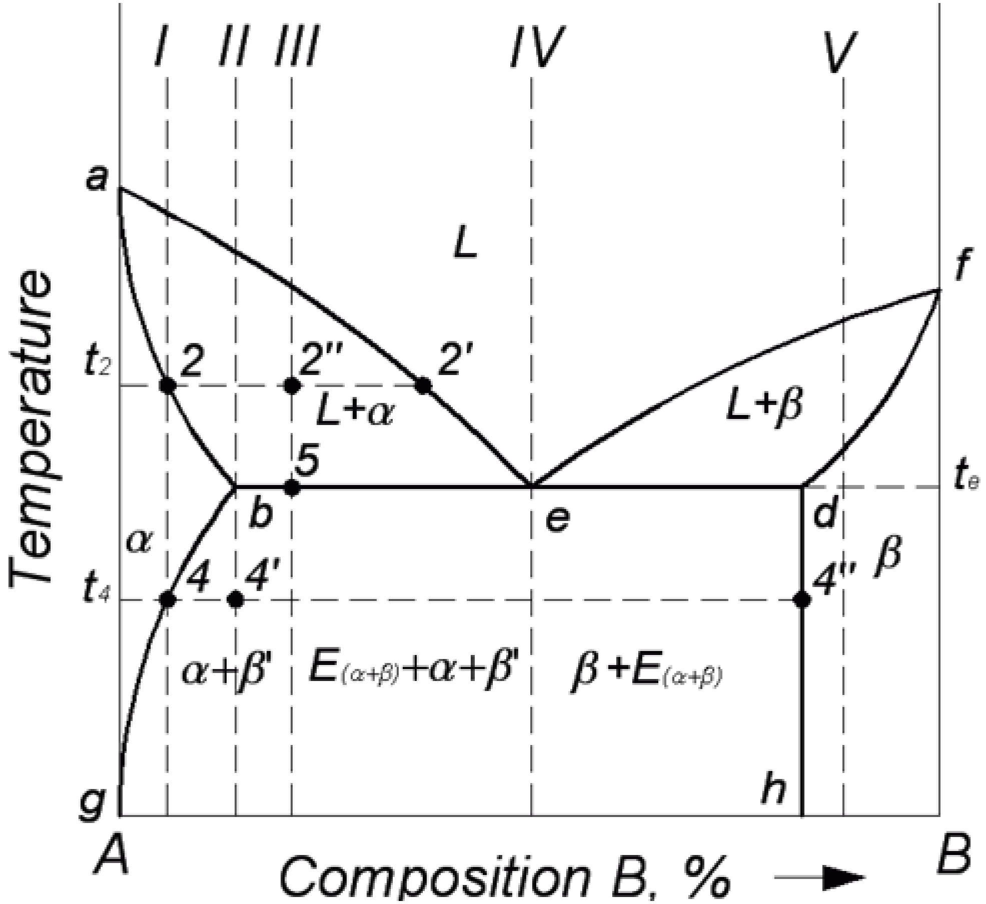




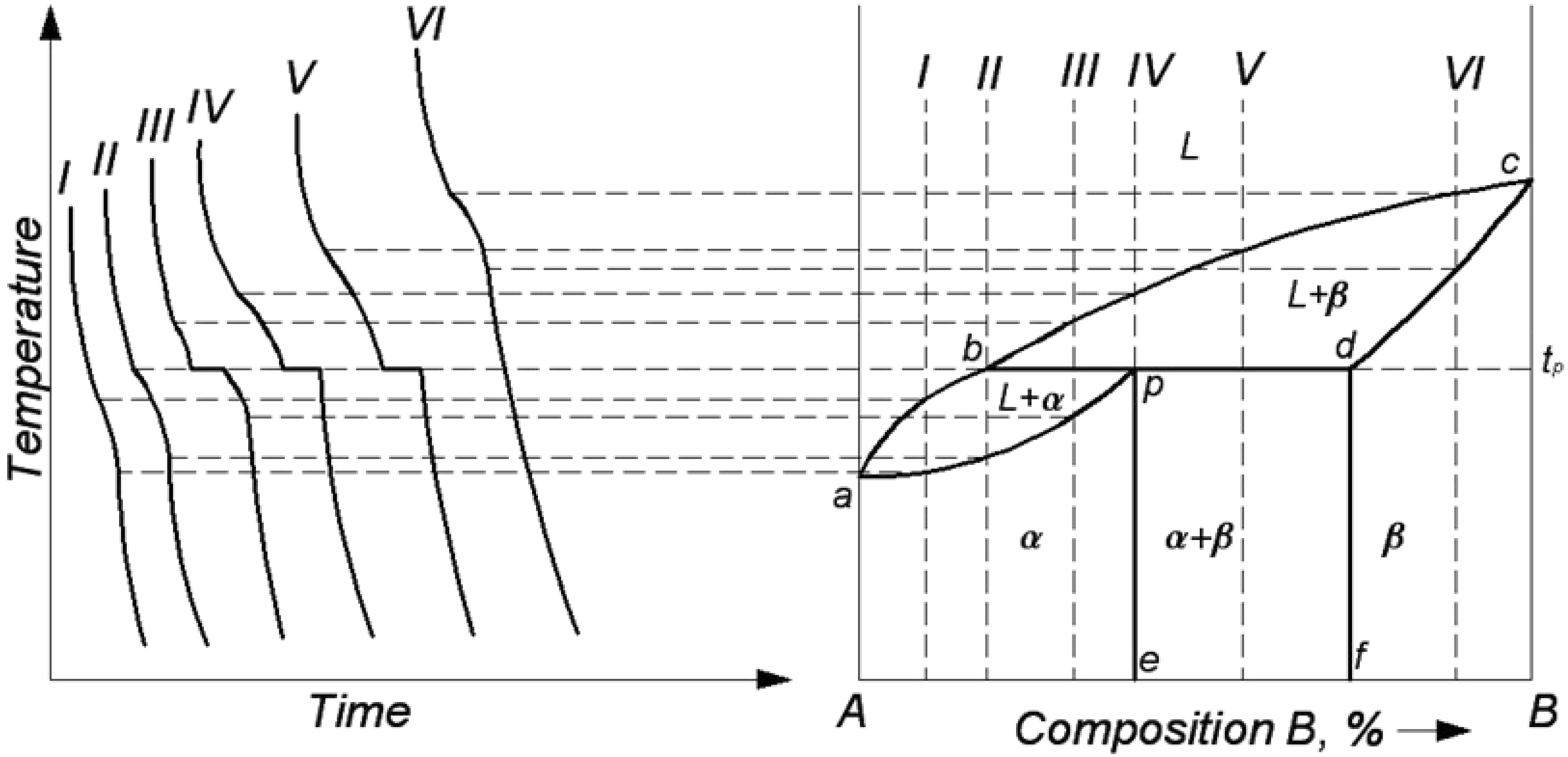
Binary systems with limited solid solubility – eutectic system



Binary systems with limited solid solubility– eutectic system

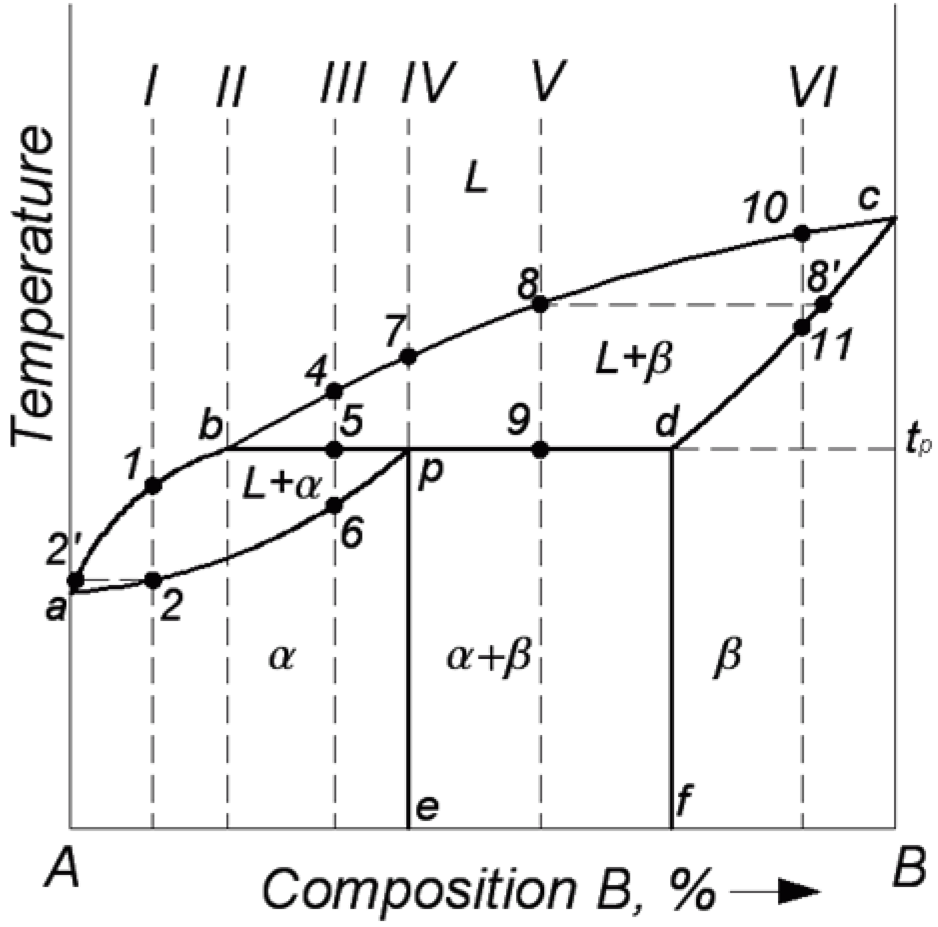


Binary systems with limited solid solubility – peritectic system

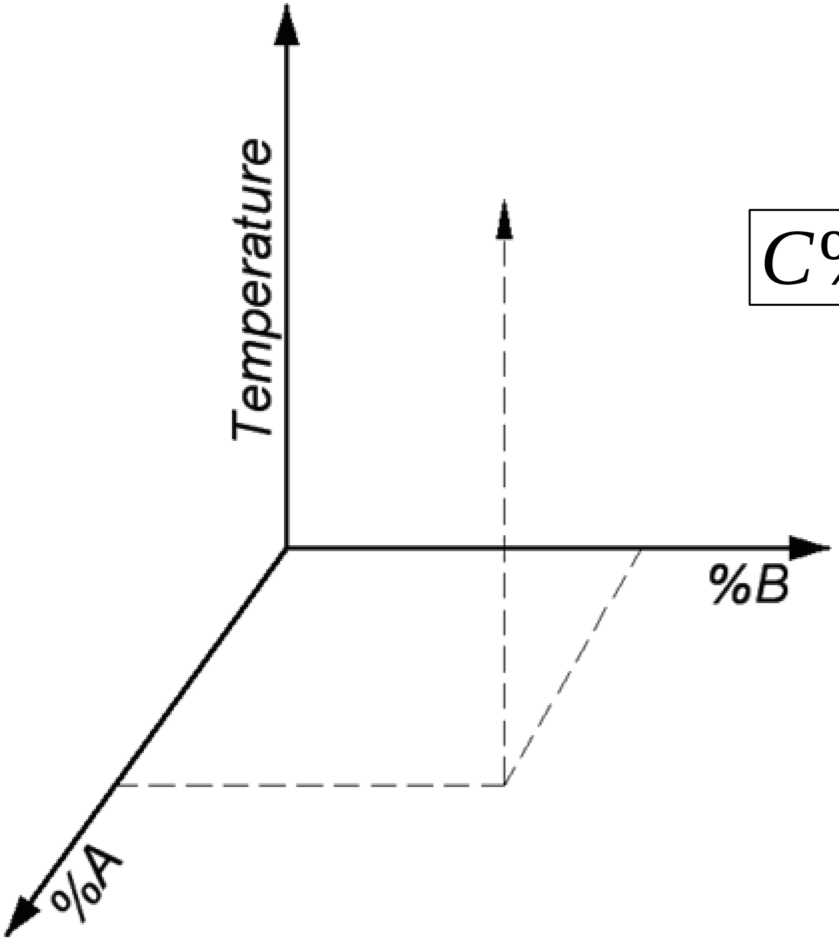


$$\beta_\alpha + L_b \underset{cooling}{\overset{heating}{\rightleftarrows}} \alpha_p$$

Binary systems with limited solid solubility – peritectic system

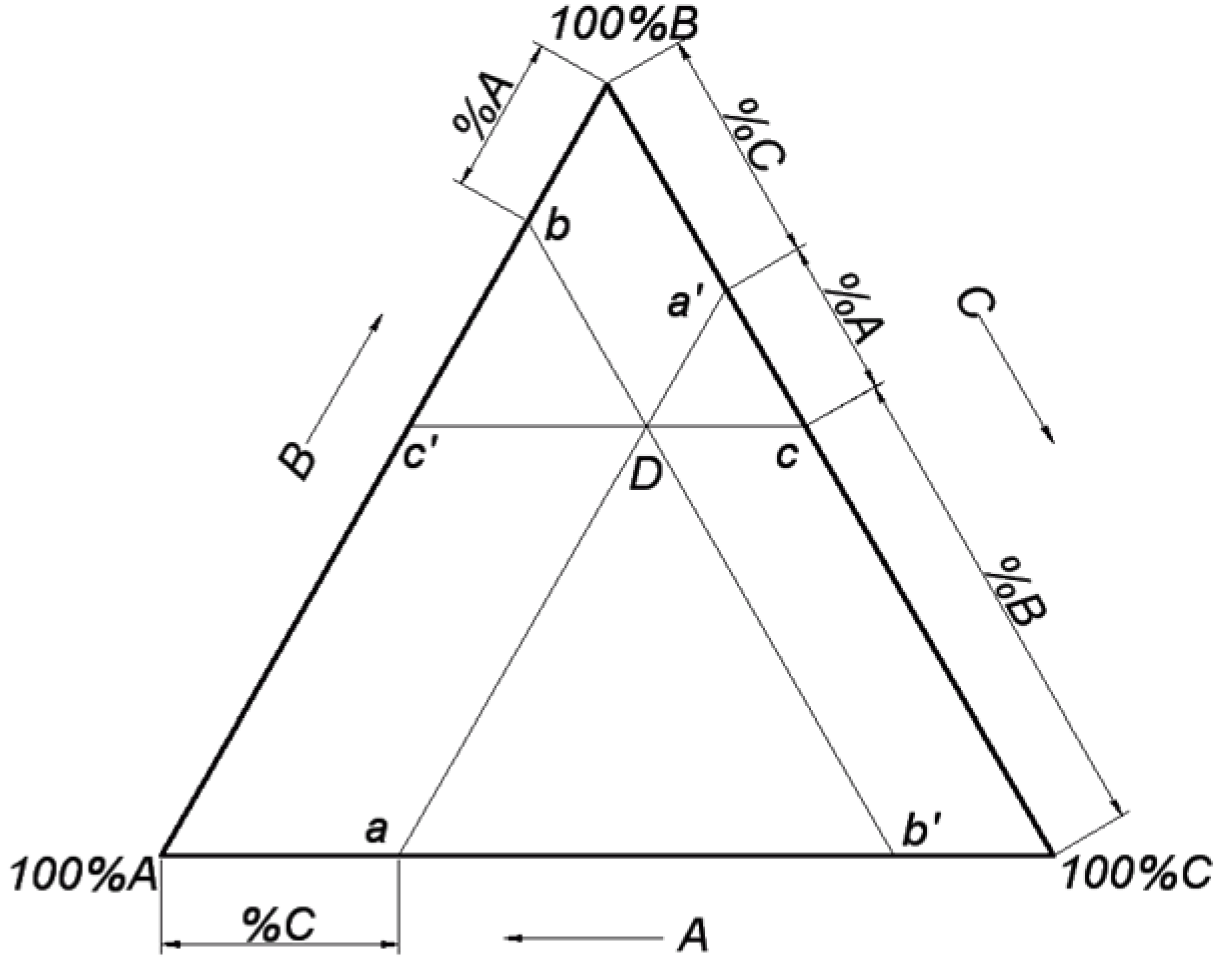


Ternary systems



$$C\% = 100\% - A\% - B\%$$

Ternary systems – composition triangle

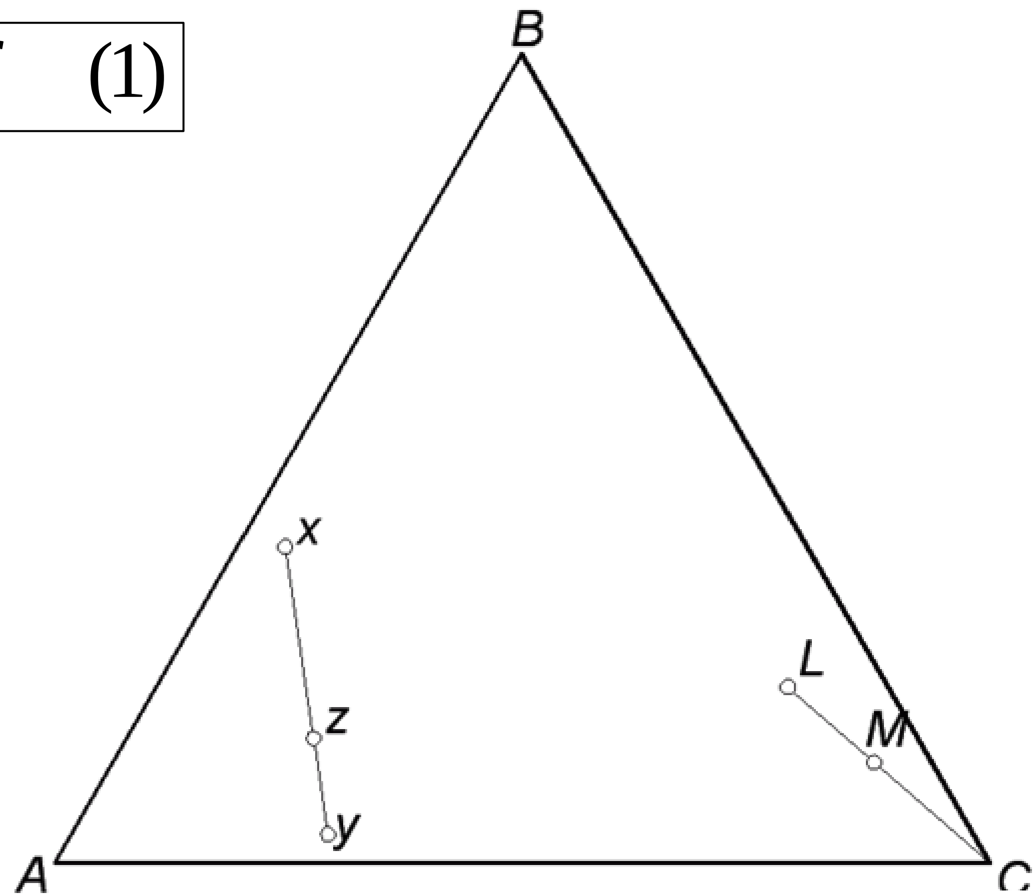


Ternary systems – segment rule

$$S = n - f + 1 = 4 - f \qquad (1)$$

$$\frac{m_x}{m_y} = \frac{y - z}{x - z} \qquad (2)$$

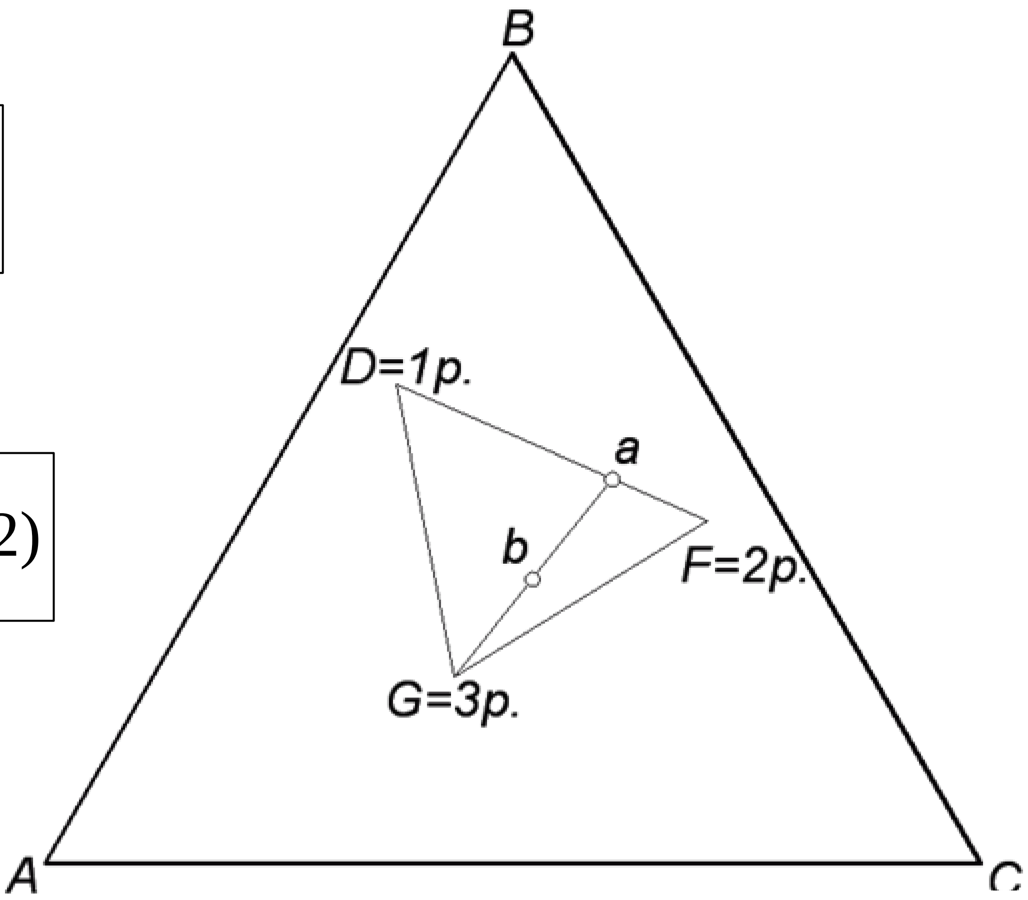
$$\frac{m_C}{m_L} = \frac{L - M}{M - C} \qquad (3)$$



Ternary systems

$$\frac{D}{F} = \frac{1}{2} = \frac{a-F}{a-D} \qquad (1)$$

$$\frac{G}{D+F} = \frac{1}{1} = \frac{a-b}{b-G} \qquad (2)$$

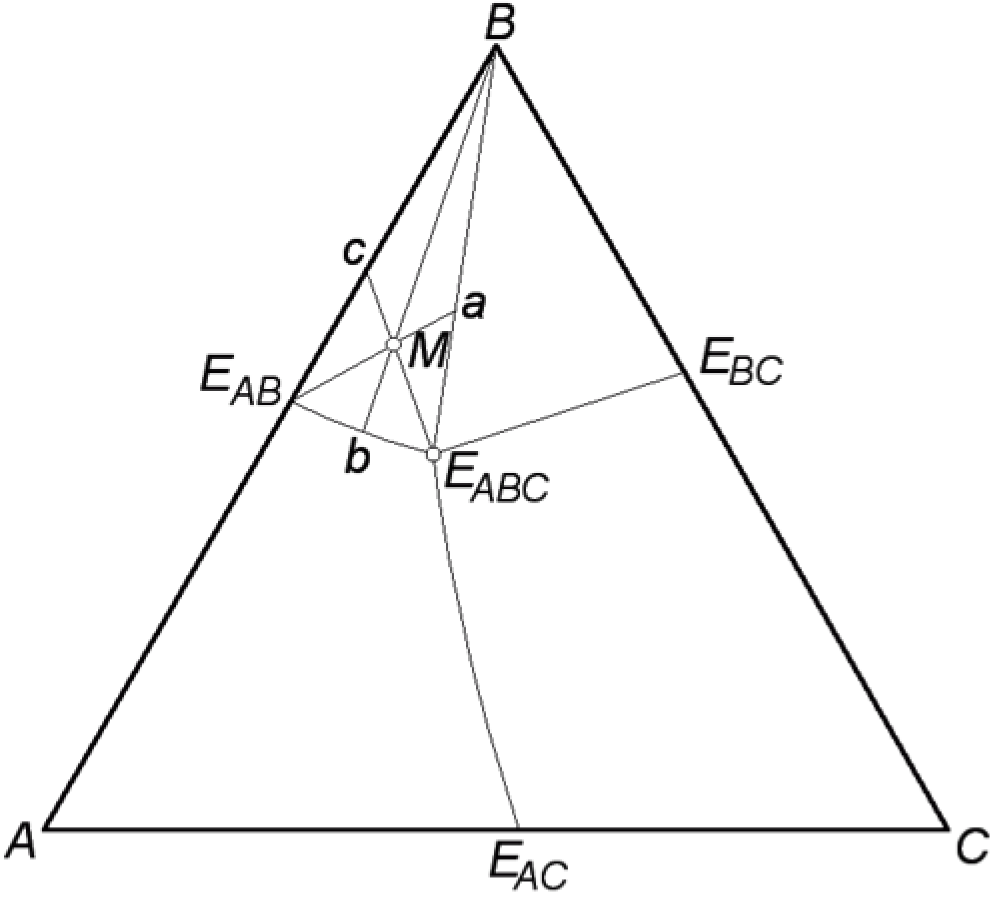


Ternary systems

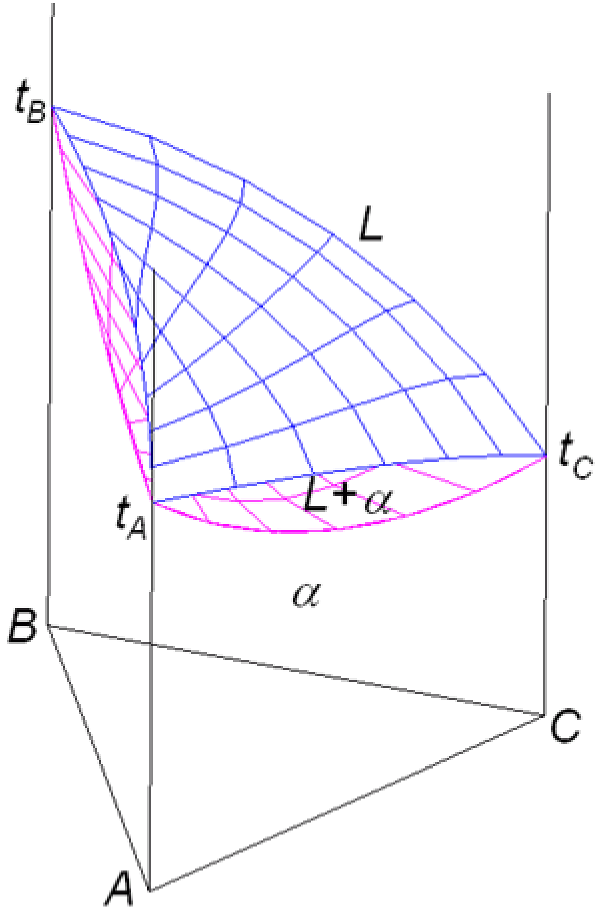
$$B = \frac{b - M}{B - b}$$

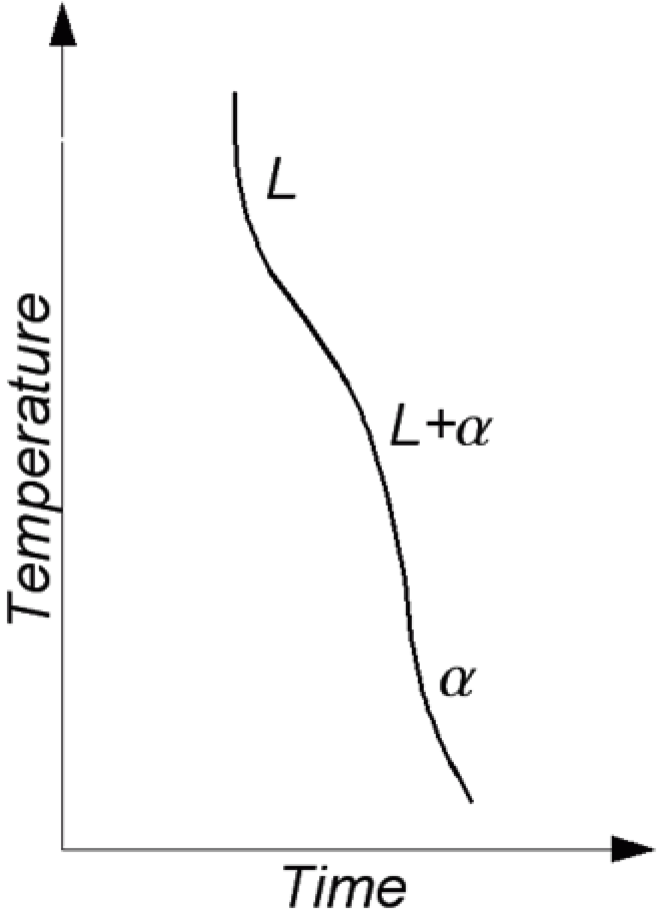
$$E_{AB} = \frac{a - M}{a - E_{AB}}$$

$$E_{ABC} = \frac{c - M}{c - E_{ABC}}$$

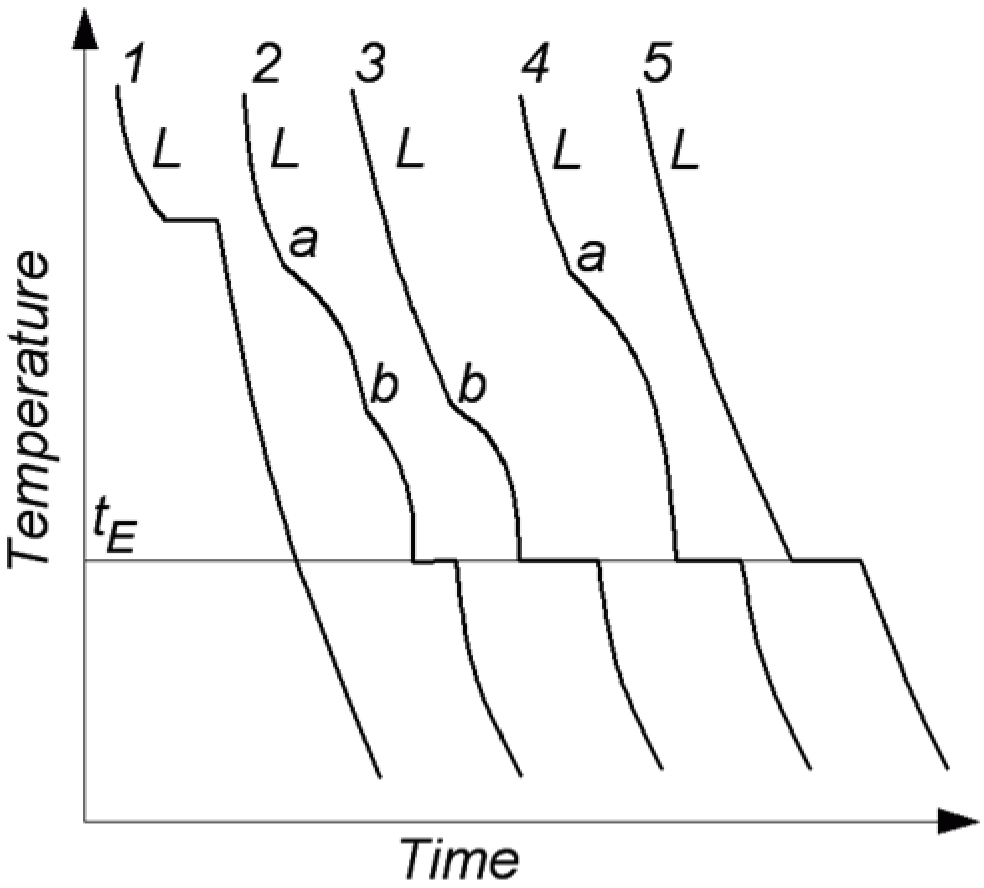


Ternary systems – isomorphous system

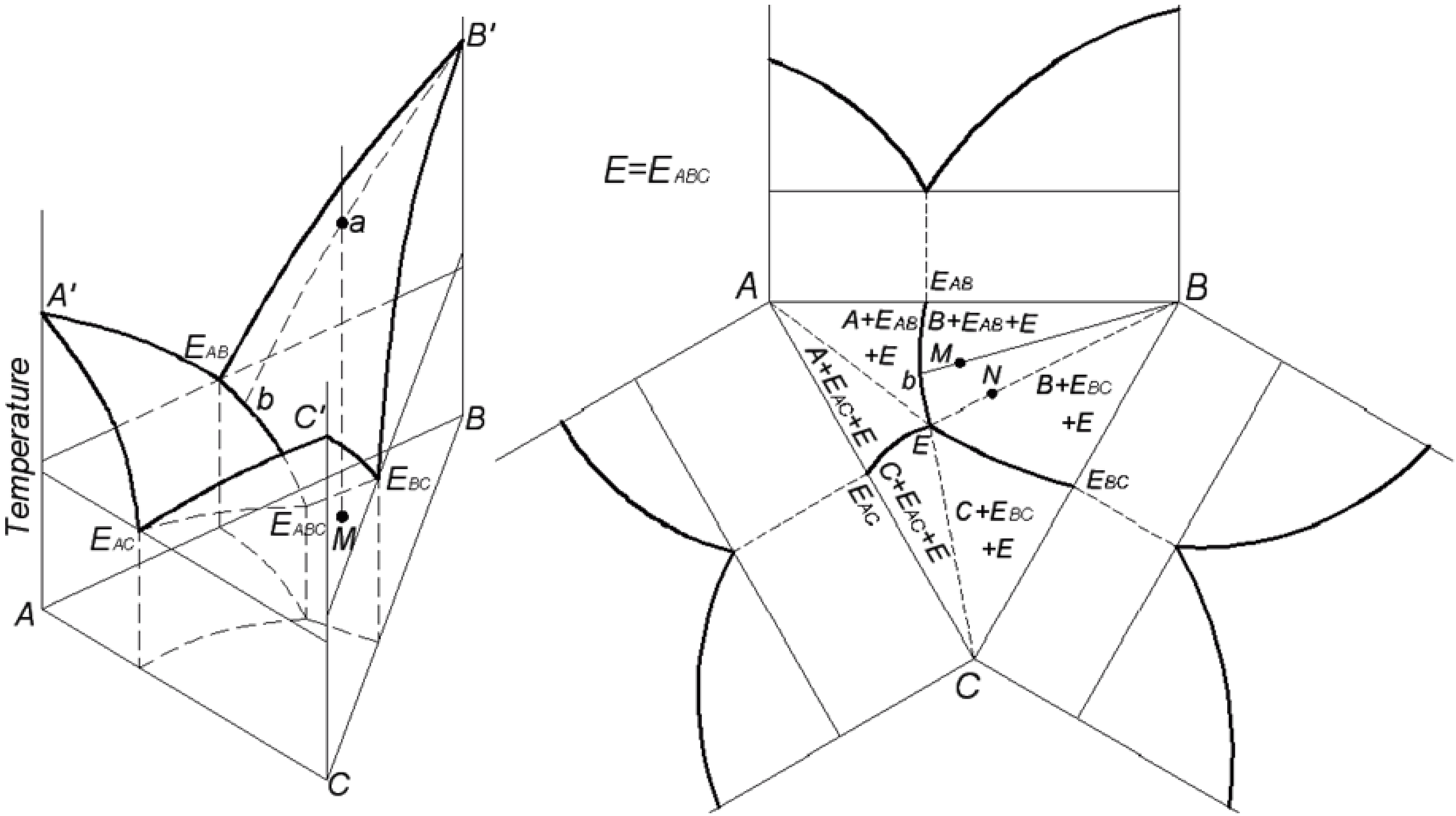




Ternary systems – eutectic system



Ternary systems – eutectic system



Summary

- Basic concepts
- Gibbs free energy
- Lever rule
- Cooling curves
- Binary phase equilibrium diagrams
- Ternary phase equilibrium diagrams

Literature

- W.D. Callister, *Material Science and Engineering: An Introduction*, John Wiley and Sons, 1999
- B. Chalmers, *Principles of Solidification,* Krieger Pub Co, 1977
- A.G. Guy, *Introduction to Materials Science,* McGraw-Hill, 1972
- W. Kurz, D.J. Fisher, *Fundamentals of solidification,* Trans Tech Publications, 1998