European Funds
Knowledge Education Development

INSTITUTE OF METALLURGY
AND MATERIALS SCIENCE
POLISH ACADAMY OF SCIENCES

European Union
European Social Fund

FUNDAMENTALS OF THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY
Application in Materials Science Investigations

Analiza cieplna i kalorymetria różnicowa w badaniach materiałów

Lecture 2.
Basic definitions and problems concerning thermal analysis and phase transitions

Project WND-POWR.03.02.00-00-I043/16

International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

Project co-financed by the European Union within the European Social Funds

FUNDAMENTALS OF THERMAL ANALYSIS

Heat transport (exchange, heat transfer)

one of the ways of energy transfer between thermodynamic systems

The exchange of heat always proceeds from a system with a higher temperature to the system of a lower temperature, according to the second law of thermodynamics, and lasts until the state of thermal equilibrium is reached.

Mechanisms of heat transport

The heat exchange takes place in one of three ways:

1) **thermal conduction** consists in transferring energy by the chaotic movement of particles and their collisions;
2) **thermal convection** (raising heat) involves the flow of thermal energy resulting from the movement of matter in the volume of fluid (liquid or gas):

- *natural (free)* - free fluid movement due to the difference in density resulting from the difference in temperature,
- *forced* - fluid movement is caused by external factors (pump, fan, etc.);

3) **thermal radiation** consists in energy transmitted by electromagnetic radiation emitted as a result of thermal motion of molecules. Heat exchange by radiation does not require the presence of a medium between the systems which exchanged heat, what can occur through the vacuum.

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Heat capacity (*C*)

a physical quantity which characterizes the amount of heat, required to change the temperature of the object by the unit of temperature

$$C = \frac{\Delta Q}{\Delta T} \quad \left[\frac{J}{K}\right]$$

ΔQ – change of heat;
ΔT – change of temperature.

The molar heat capacity is the heat capacity per mole of pure substance.

Specific heat capacity (also referred to as **specific heat, Cp**) is the heat capacity per unit weight of the substance.

$$C_p = \frac{\Delta Q}{m\Delta T} \quad \left[\frac{J}{gK}\right]$$

ΔQ – change of heat;
ΔT – change of temperature;
m – weight of the substance.

FUNDAMENTALS OF THERMAL ANALYSIS

Heat capacity (*C*) cont.

intense parameter, what means that it is not dependent on the amount, but the type of material.

It may also depend on the temperature, therefore the equation in differential form is more precise :

$$C_p(T) = \frac{1}{m}\left(\frac{dQ}{dT}\right)$$

Thermal properties of solids

Thermal expansion

the objects ability to reversibly change size (length - linear expansion, volume - volumetric expansion) under the influence of temperature changes

$$\alpha = \frac{1}{l_0}\frac{dl}{dT}$$

Linear coefficient of thermal expansion

l – lenght, T - temperature

$$\gamma = \frac{1}{V_0}\frac{dV}{dT}$$

Volume coefficient of thermal expansion

V - volume, T - temperature

Thermal properties of solids

Thermal expansion of selected groups of materials

Single crystals of regular crystallographic structure expands in all directions uniformly – *isotropy of properties*.

Single crystals of crystallographic structure other than the regular and multiphase materials, have different coefficients of thermal expansion for the various directions - *anisotropy of properties.*

Metals, due to their high thermal conductivity, are characterized by high thermal expansion and no type of II stresses.

Ceramic materials are characterized by low (or zero) thermal expansion and the occurrence of type II stresses.

Phase transformations

Phase transformation (phase transition)

thermodynamic process, consisting in transformation the specific, defined thermodynamic phase into another one, occurring in the direction ensuring minimization of the free energy of the system and thermodynamic equilibrium

Phase transformations

Classification of phase transformations

1. of the I-st type – in relation to the state of matter:

- leads to a change in the state of matter, e.g. evaporation and condensation, crystallization and melting, sublimation and resublimation,
- occurs without changing the physical state, in solid or liquid phase, e.g. allotropic transformation.

2. of the II-nd type – in relations to the mechanism of transformation:

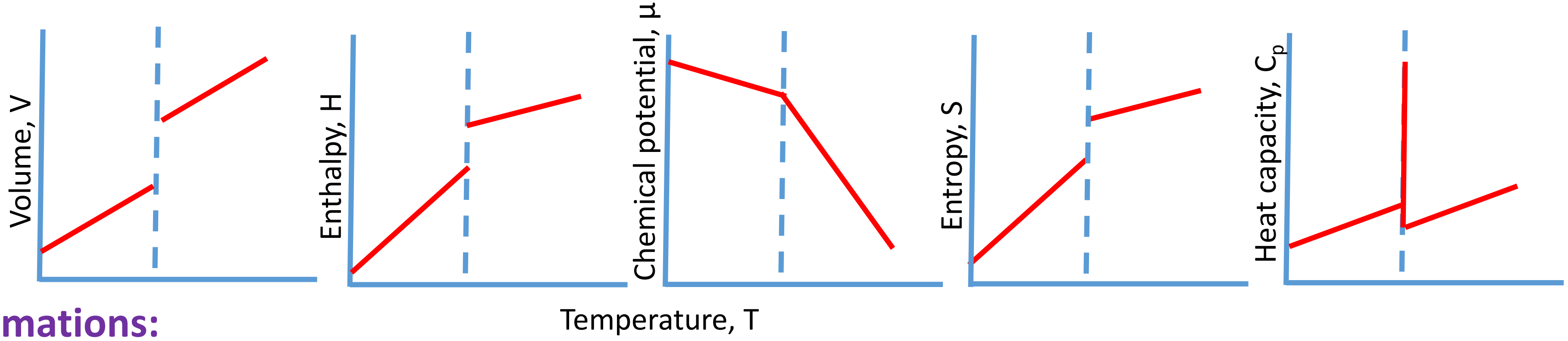
- *diffusional* - their course is associated with mass transport (for short or long distances), e.g. eutectoid transformation, separation of components from supersaturated solid solutions,
- *non-diffusional* - not requiring mass transport, e.g. martensitic transformation.

Phase transformations

Classification of phase transformations cont.

3. of the III-rd type – in relations to thermodynamics *(Paul Ehrenfest classified phase transitions based on the behavior of the thermodynamic free energy as a function of other thermodynamic variables)*:

- **transformations of the first order** in which a discontinuous (step) change in state functions takes place (eg volume (density), entropy, internal energy and enthalpy of the system) at thermodynamic equilibrium temperature, which is associated with heat release or absorption (latent heat).



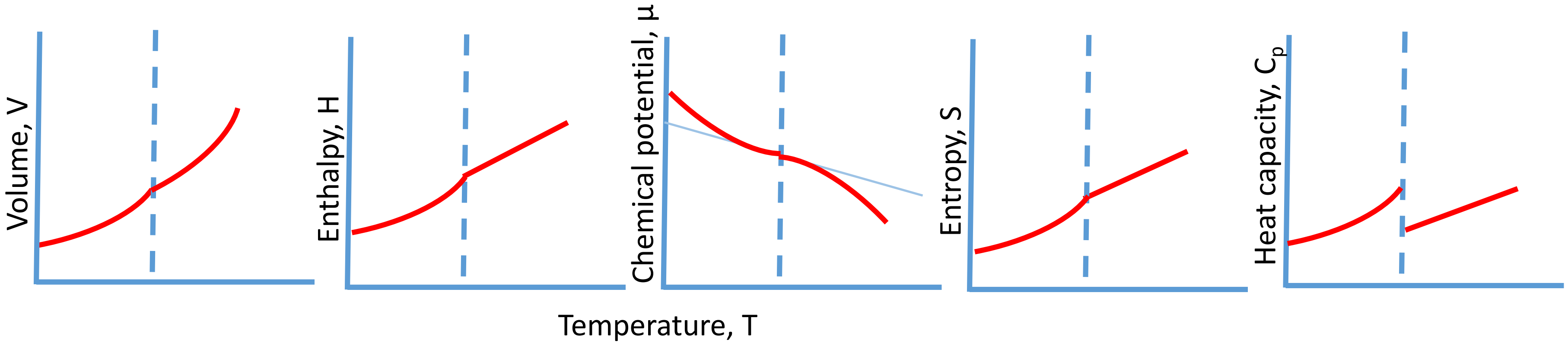
1-st order transformations:

- polymorphic,
- melting,
- sublimation,
- crystallization,
- transition to the superconducting state in a magnetic field.

Phase transformations

Classification of phase transformations cont.

- ***transformations of the second order*** in which a continuous change of parameters take place. The derivatives (heat capacity, thermal expansion coefficient) remain discontinuous. There is no thermal effect here.



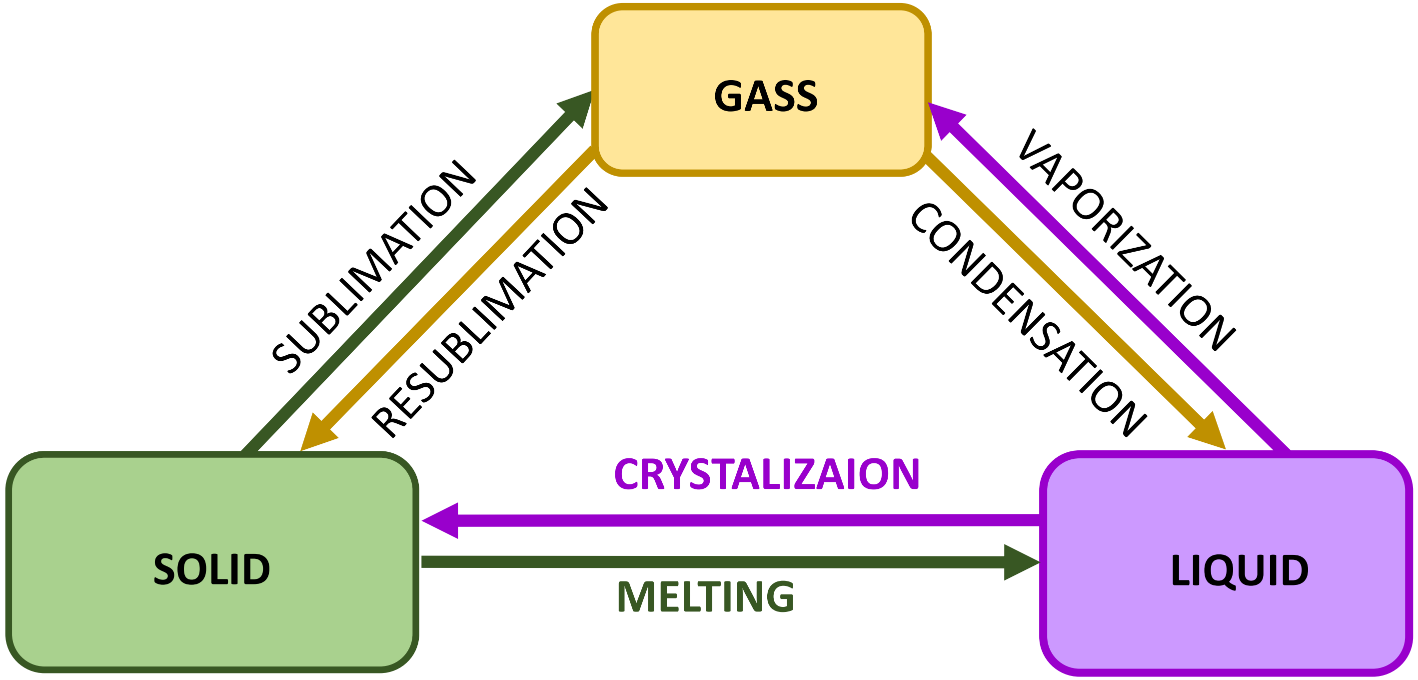
2nd order transformations:

- magnetic transformations in ferromagnetic metals,
- transition to superconductivity without a magnetic field,
- helium change into a superfluous variety,
- change of order-disorder.

Examples of phase transformations of the first order

Phase transformations of the first order are always accompanied by absorption or release of heat. These are transformations in which the state of matter or crystal structure changes.

The diagram illustrates transitions between the three fundamental states of matter



Examples of phase transformations of the first order

change of the matter state

Melting

Melting point is the temperature at which the substance in the solid state is in equilibrium with the liquid phase at constant pressure.

The dependence of melting point on pressure is determined by the **Clausius-Calpeyron** law:

$$\frac{dT}{dp} = T_0 \frac{(V_2 - V_1)}{\Delta H}$$

V_1, V_2 - molar volume of substances in solid and liquid state.

$V_2 > V_1$ ⇒ the melting temperature increases with increasing pressure

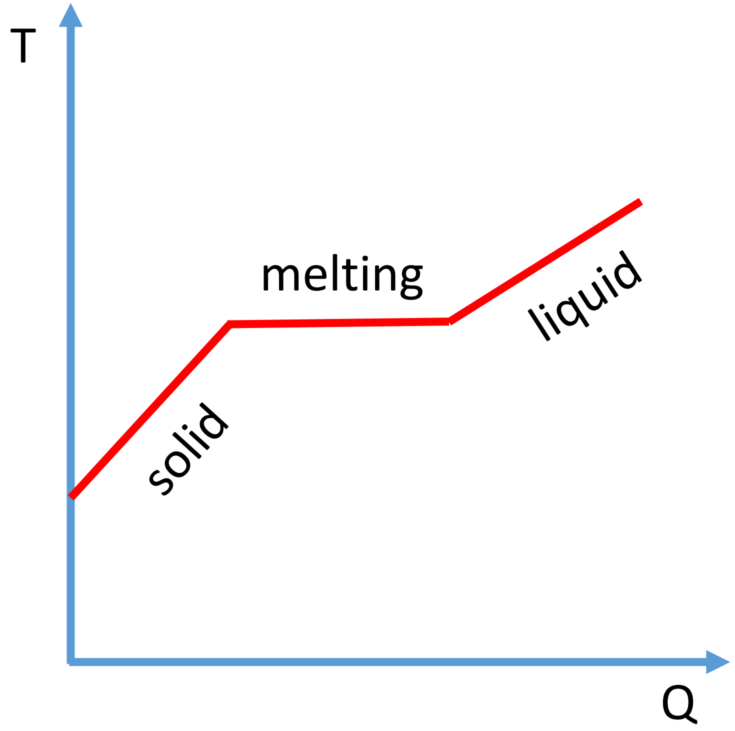
The increase in the specific volume during melting process takes place for most solids

EXCEPTIONS: ice, lead, bismuth, tin

Melting is an **endothermic** process = it is accompanied by **heat absorption** (***C_m***)

Examples of phase transformations of the first order

change of the matter state



the heat **Q** needed to melt the solid mass **m** is:

$$Q = m \cdot C_m \qquad (J/kg)$$

Examples of phase transformations of the first order

change of the matter state

Crystallization

the process of formation of a crystalline phase from the solid (amorphous) phase, the liquid phase or the solution

Crystallization is an exothermic process, which is accompanied by the release of heat (C_c)

For a given substance, the amount of heat to be delivered to the melt is equal to the amount of heat released by this substance in the crystallization process.

$$C_c = C_m$$

C_c – heat of crystallization
C_m – heat of melting

Examples of phase transformations of the first order

change of the crystal structure

Eutectic transition

a reversible phase transition, whereby a mixture of two solid phases (eutectics) is separated from the eutectic liquid during cooling. In the case of certain systems with a given chemical composition the transformation occurs at a ***specific temperature****, called* ***eutectic temperature****.*

At the transition temperature isothermal jump in the enthalpy vs. temperature curve is observed.

$$L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \alpha + \beta$$

L – liquid
α, β – solid phases

Examples of phase transformations of the first order

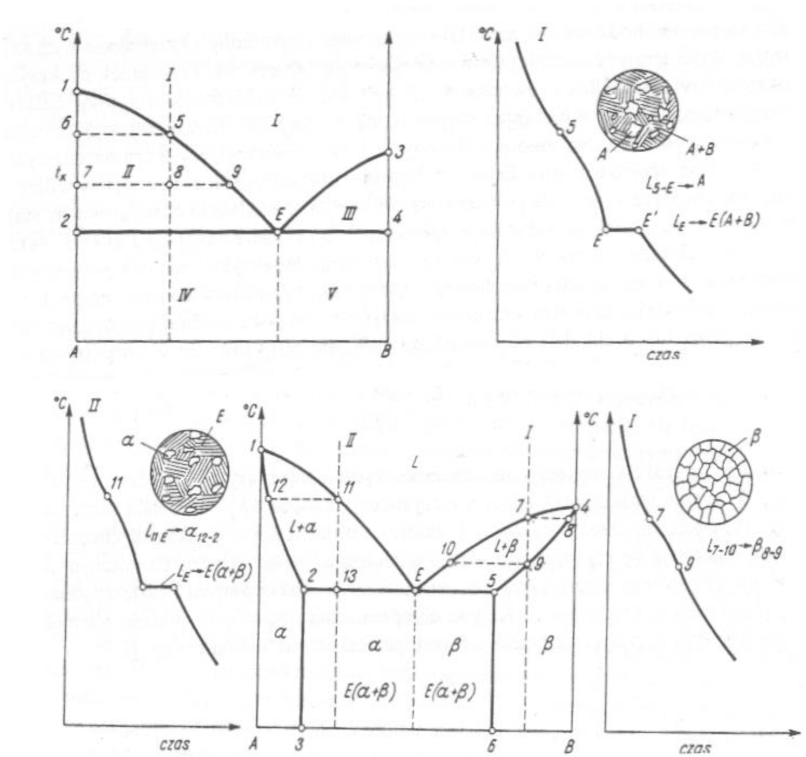
change of the crystal structure

Eutectic transformation cont.

Eutectic transformation occurs in systems whose components are characterized by:

- full solubility in the liquid and exhibit no solubility in the solid state

- full solubility in the liquid and exhibit limited solubility in the solid state

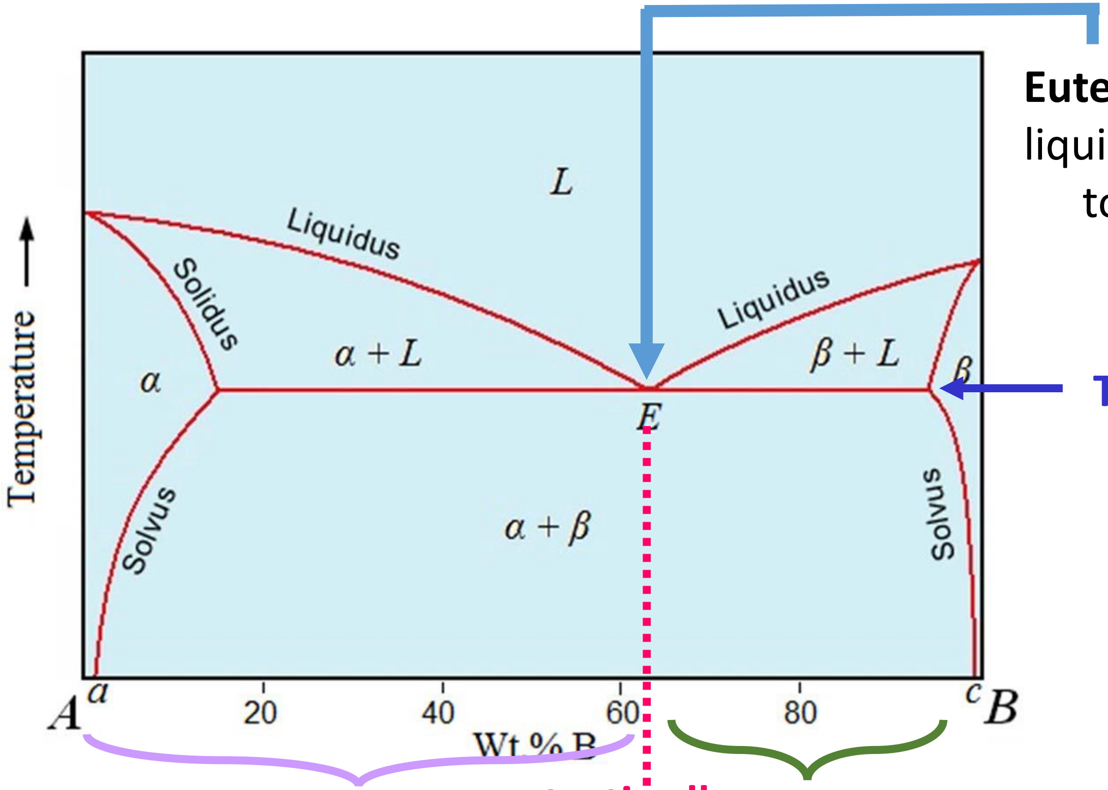


Examples of phase transformations of the first order

change of the crystal structure

Eutectic reaction c.d.

named **invariant reaction**, because it proceeds at **thermal equilibrium** (the change in ***Gibbs free energy equals zero***)



Eutectic point: Where meet 2 liquidus lines (pt. E) - referred to as an invariant point.

T_E temperature of eutectic reaction

eutectic alloy

hypoeutectic alloy

hypereutectic alloy

Examples of phase transformations of the first order

change of the crystal structure

Peritectic transition

a reversible phase transition, whereby a new solid phase (peritectic) is released during cooling from a liquid and a solid phase with a peritectic composition. For specific systems with a given chemical composition it occurs at a ***specific temperature****, called* ***peritectic temperature***

At the transition temperature isothermal jump in the enthalpy vs. temperature curve is observed.

$$L + \alpha \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \beta$$

L – liquid
α, β – solid phases

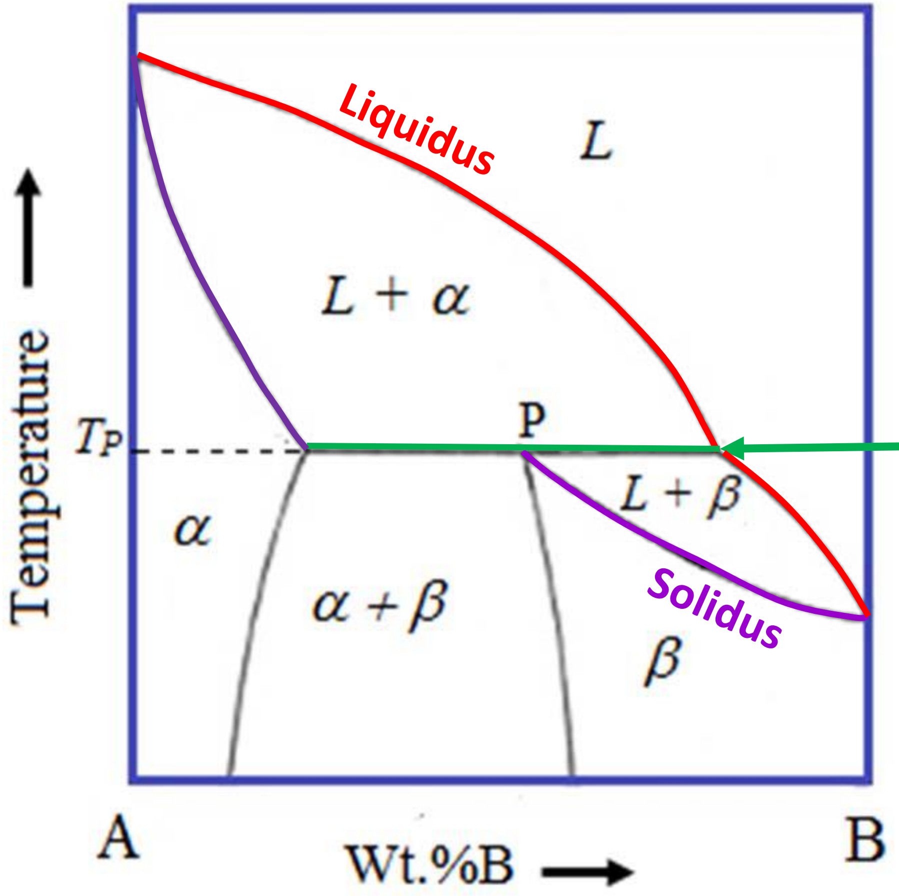
It occurs in systems in which components are characterized by full solubility in the liquid and exhibit limited solubility in the solid state

Examples of phase transformations of the first order

change of the crystal structure

Peritectic reaction c.d.

named **invariant reaction**, because it proceeds in **thermal equilibrium** (the change in ***Gibbs free energy equals to zero***)



T_P temperature of peritectic reaction

Examples of phase transformations of the first order

change of the crystal structure

Eutectoid transformation

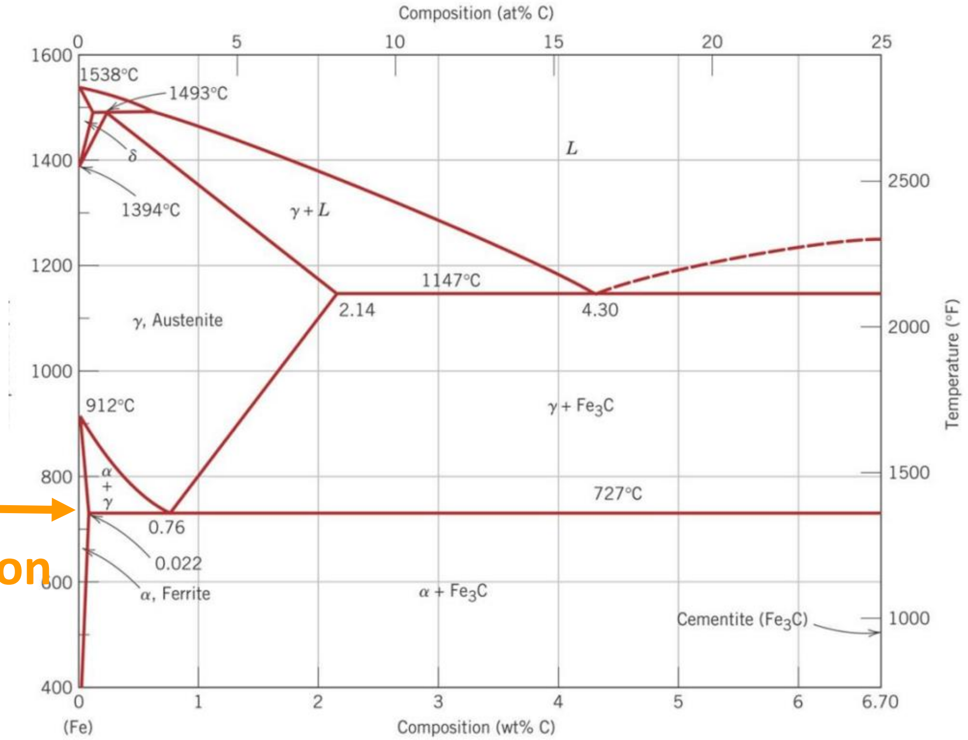
a reversible phase transition, whereby a mixture of two solid phases (eutectoid) is isolated during cooling from a solid phase with eutectoid composition. For certain systems with a given chemical composition it occurs at a ***specific temperature****, called* ***eutectoid temperature***

$$\gamma \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \alpha + \beta$$

γ, α, β – solid phases

invariant reaction!

Temperature of eutectoid reaction



Examples of phase transformations of the first order

change of the crystal structure

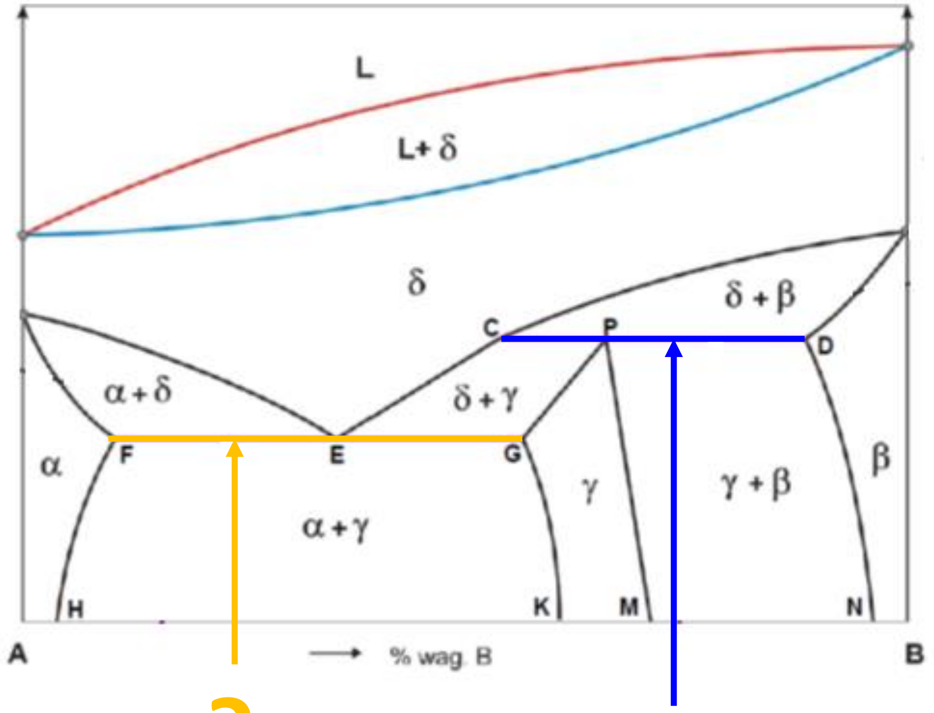
Peritectoid transformation

*a reversible phase transition, whereby a new solid phase is released during cooling of two solid phases with a peritectic composition. For certain systems with a given chemical composition, it occurs at a **specific temperature**, called **peritectoid temperature***

$$\gamma + \alpha \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \beta$$

γ, α, β – solid phases

invariant reaction!



?

Temperature of peritectoid reaction

Examples of phase transformations of the second order

Phase transformations of the second order are accompanied neither by absorption nor release of the heat.

The enthalpy of conversion is zero.

2nd order transformations:

- magnetic transformations in ferromagnetic metals,
- transition to superconductivity without a magnetic field,
- helium change into a superfluous variety,
- change of order-disorder.

Examples of phase transformations of the second order

Glass transition

Phase transition of the second type characterized by:

- *it is not accompanied by a measurable energetic thermal effect,*
- *a sudden change in thermal capacity is observed.*

Glass transition temperature (symbol: T_g) - the temperature at which the transition from the liquid or solid state into a glassy state appears during very fast cooling process. It is manifested by a stepwise increase in viscosity of the substance. It can be determined as the point of inflection on thermogram revealing the change of thermal capacity with temperature. In practice, the glass transition temperature is most often determined by differential scanning calorimetry.

Some history in the field of thermal analysis

1887 – French chemist ***Henry Louis Le Chatelier*** (1850-1936) carries out the first thermoanalytical measurement

1899 – ***William Chandler Roberts-Austen*** (1843-1902) is recognized as the discoverer of differential temperature analysis (DTA)

1915 – Japanese metallurgist ***K. Honda*** published the results of the first thermogravimetric analysis (TGA) with a constant mass measurement

1955 – ***S. L. Boersma*** developed the principles of today's heat flow differential scanning calorimetry (DSC)

Thermal analysis

Thermal analysis

Thermal analysis is a widely used experimental measurement technique with a long history. It is a branch of materials science, which let to determine the physical and chemical properties of materials versus the temperature changes in time

The scope of research in thermal analysis:

- changes in material properties during heating or cooling;
- phase transitions;
- determination of the chemical and / or phase composition of materials;
- determination of thermodynamic and kinetic parameters of the reaction;
- determination of materials purity and homogeneity;
- determination of specific heat and heat of phase transformations;
- determination of water and moisture content;
- determine the thermal stability of materials.

Thermal analysis

Examinated materials:

- metals and metal alloys;
- organic substances;
- ceramics;
- polymers;
- pharmacological agents;
- food.

Measured parameters:

- change in sample weight;
- sample and furnace temperature;
- heat absorbed and released;
- dimensions of the sample;
- thermal conductivity;
- thermal capacity.

Thermal analysis – methods classification

Types of the thermal analysis methods in relation to:

1) ***method of the sample heating***

STATIC - the temperature of the sample is changed in steps and it is kept at a given level until the sample components reach equilibrium, specific for this temperature.

DYNAMIC - sample temperature is changed in a linear way.

Thermal analysis – methods classification

2) measured parameter

Method	Abbreviation	Measured parameter	Application
Thermal analysis	TA	Temperature	Temperature of phase transformations
Differential thermal analysis	DTA	Temperature difference versus temperature or time	Temperature range of the phase transformation or chemical reaction
Thermogravimetric analysis	TGA	Mass change versus temperature or time	Processes with the mass changes: decomposition, oxidation, synthesis
Differential scanning calorimetry, heat flux type	DSC	Heat flow changes versus temperature or time	Temperature range of phase transformation or chemical reaction, enthalpies of transformations, thermal capacity
Differential scanning calorimetry, compensation	DSC	Compensated heat flow	
Differential scanning calorimetry, pressure	PDSC	Heat flow at elevated hydrostatic pressure	
Thermomechanical analysis and Dynamic thermomechanical analysis	TMA and DTMA	Dimensional changes versus temperature or time and Measures storage modulus (stiffness) and loss modulus (damping) versus temperature, time and frequency	Thermal expansion, phase transitions, deformability, deflection
Thermodilatometry	DL	Dimensions changes with temperature change	Phase transitions, sintering, oxidation; Ceramics, superhard, high-temperature stable materials

Thermal analysis – methods classification

*2) **measured parameter** cont.*

Method	Abbreviation	Measured parameter
Evolved gas analysis	EGA	Analysis of gases evolved during heating of a material, usually decomposition products
Dielectric thermal analysis	DEA	Dielectric permittivity and loss factor

Complex methods of thermal analysis

Modern equipment for thermal analysis enables simultaneous recording of two signals. So, we are talking about complex methods:

- ***Simultaneous techniques*** - include testing of the sample at the same time, with two or more measuring techniques, eg. simultaneous DTA-TG, DSC-TG analysis (mass change effects correlated with thermal effects occurring in the material).

- ***Simultaneous conjugate techniques*** - include testing of the sample using two or more instrumental techniques working independently, where both devices are connected by a "connector", e.g. DSC-TG-MS (mass spectroscopy), DSC-TG-FTIR.

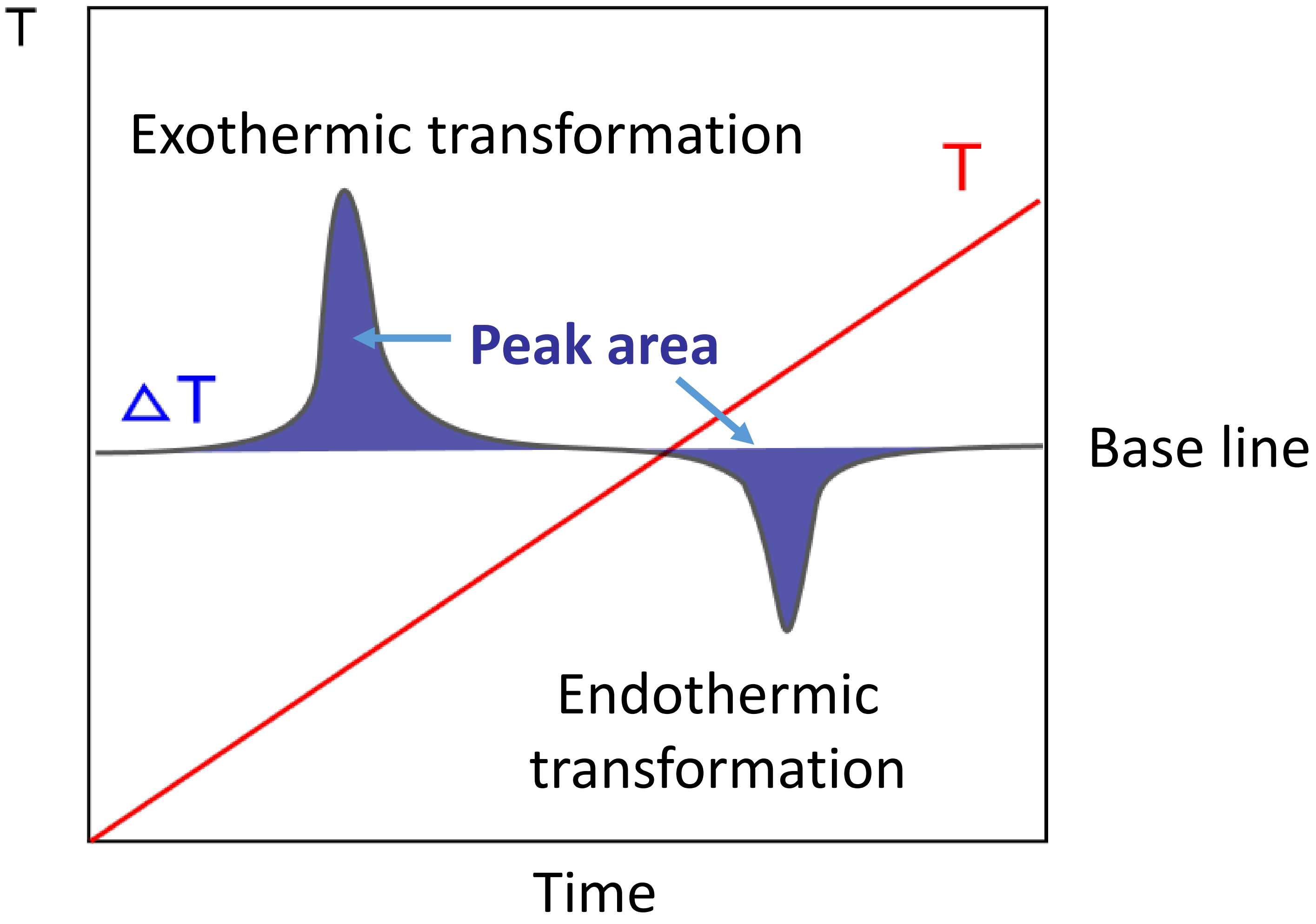
- ***Simultaneous co-operative techniques*** - include testing of the sample using two or more measurement techniques, the substance taken for testing for the other technique or the measurements are discontinuous. An example is DTA and gas chromatography - for the chromatographic analysis, appropriate portions of volatile reaction products are emitted from the test sample, which is placed in the apparatus for the first of these methods.

Results achieved by thermal analysis

The results of thermal methods are presented in the form of ***curves*** illustrating the dependence of the measured property on the temperature.

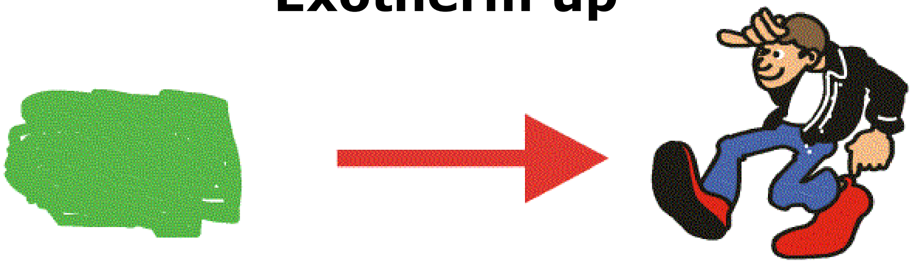
Sometimes their first derivatives are recorded - the differential curve, which determine the rate of change of the measured parameter, facilitating the distinction between overlapping thermal effects and accurate determination of the temperature of extreme points on thermal curves.

Results of the thermal analysis



Results of the thermal analysis

Exotherm up



sample

heat flux

observer

Exotherm down

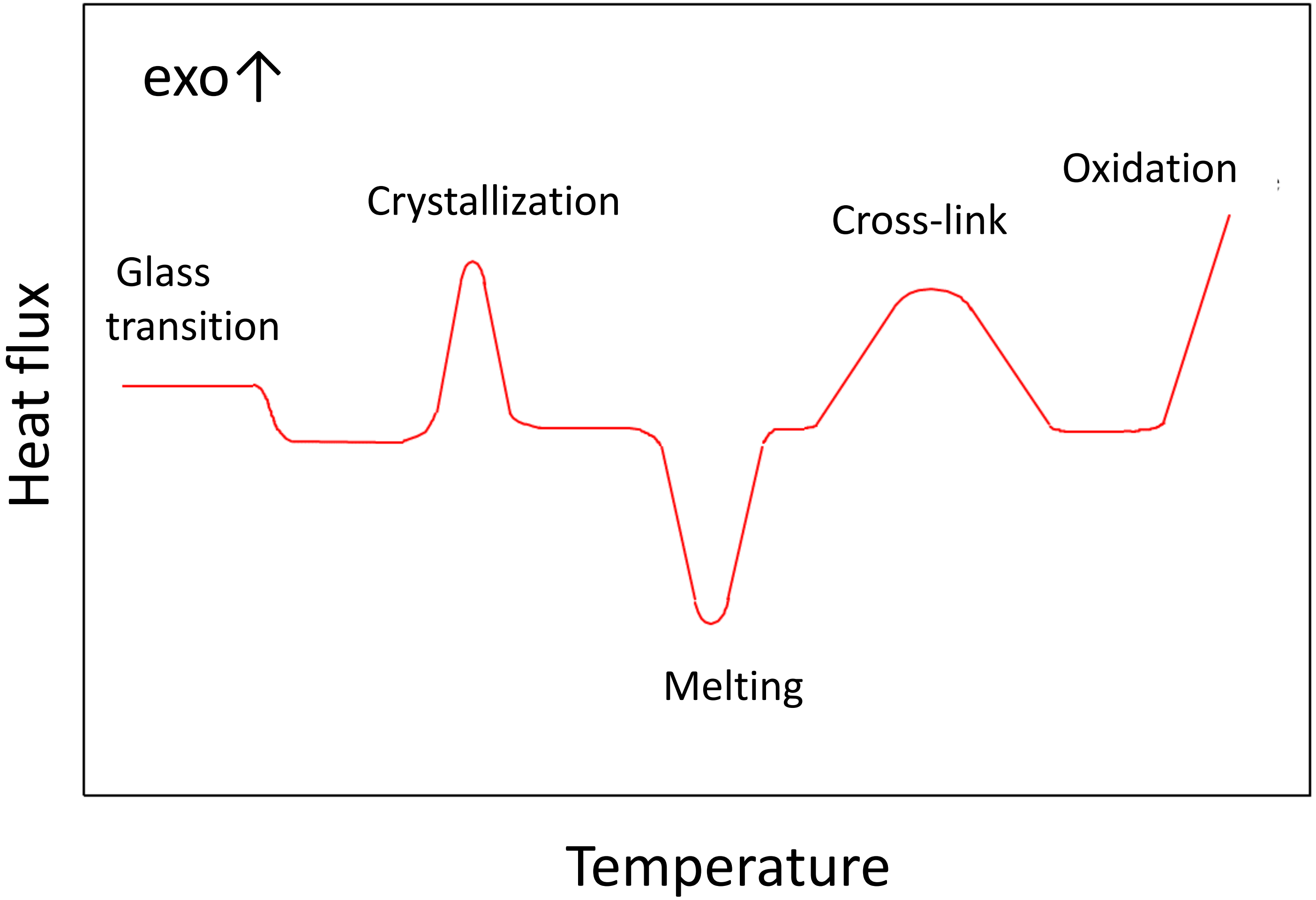
observer

sample

heat flux

environment

Results of the thermal analysis

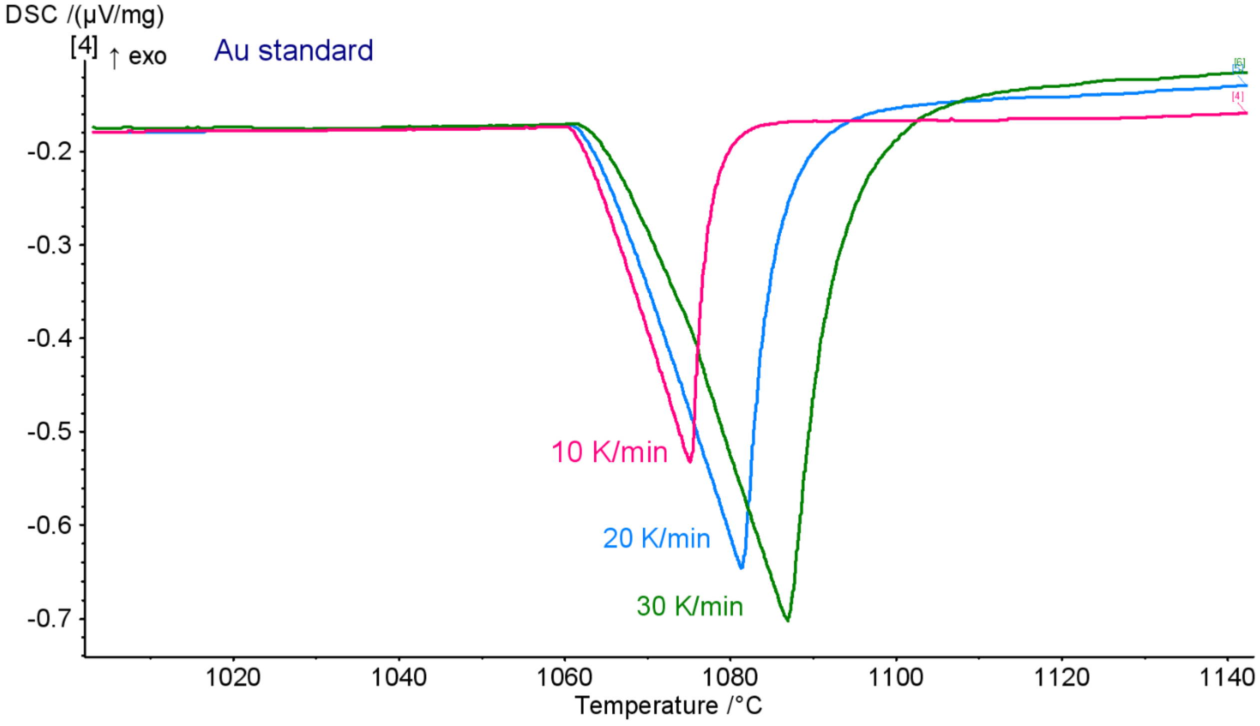


Factors affecting the shape and position of the peak

Heating rate

An increase in the heating rate causes the increase of the peak height and its broadening.

For activated process, the increase of the heating rate causes the shift of the peak maximum/minimum to higher temperatures.



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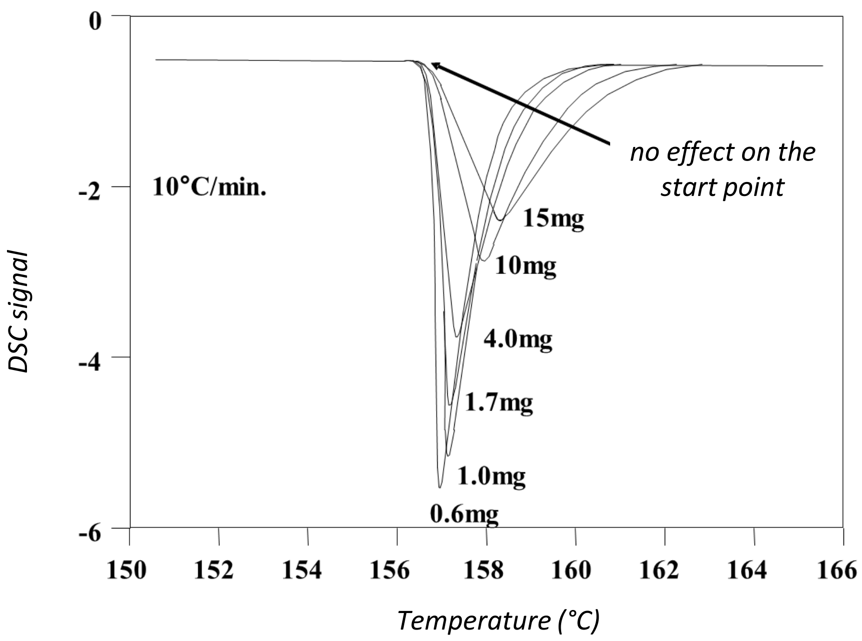
Factors affecting the shape and position of the peak

Sample mass

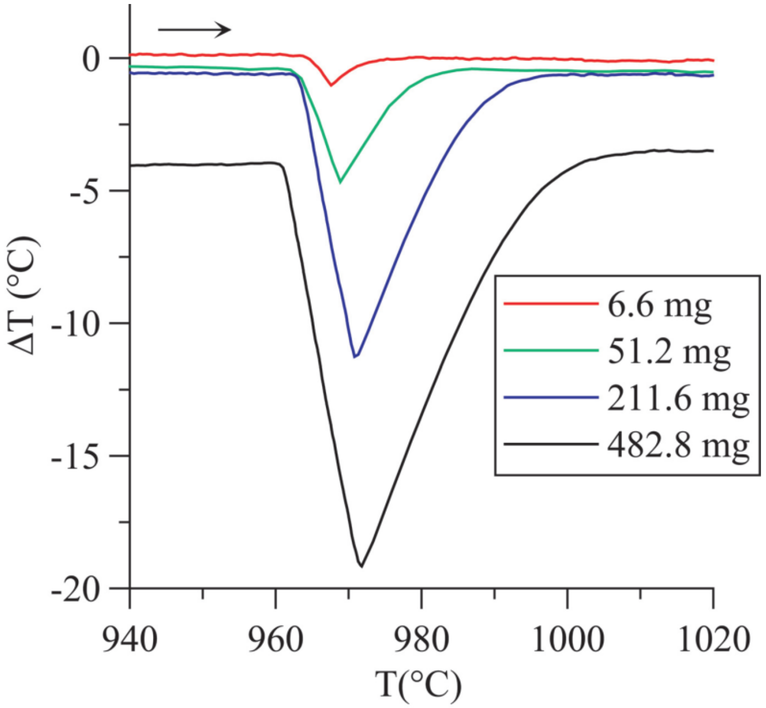
DSC



no effect on the start point

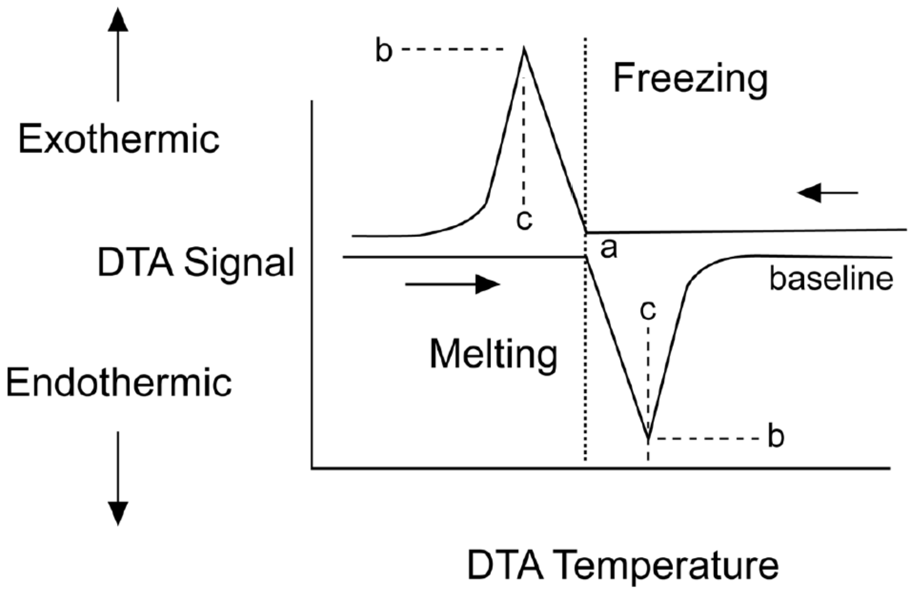
The increase in the sample mass causes: decreasing the height of the peak, its broadening and shifting peak maxima to higher temperatures.

DTA



The increase in the sample mass causes: increasing the height of the peak, its broadening and shifting peak maxima to higher temperatures.

Curve analysis



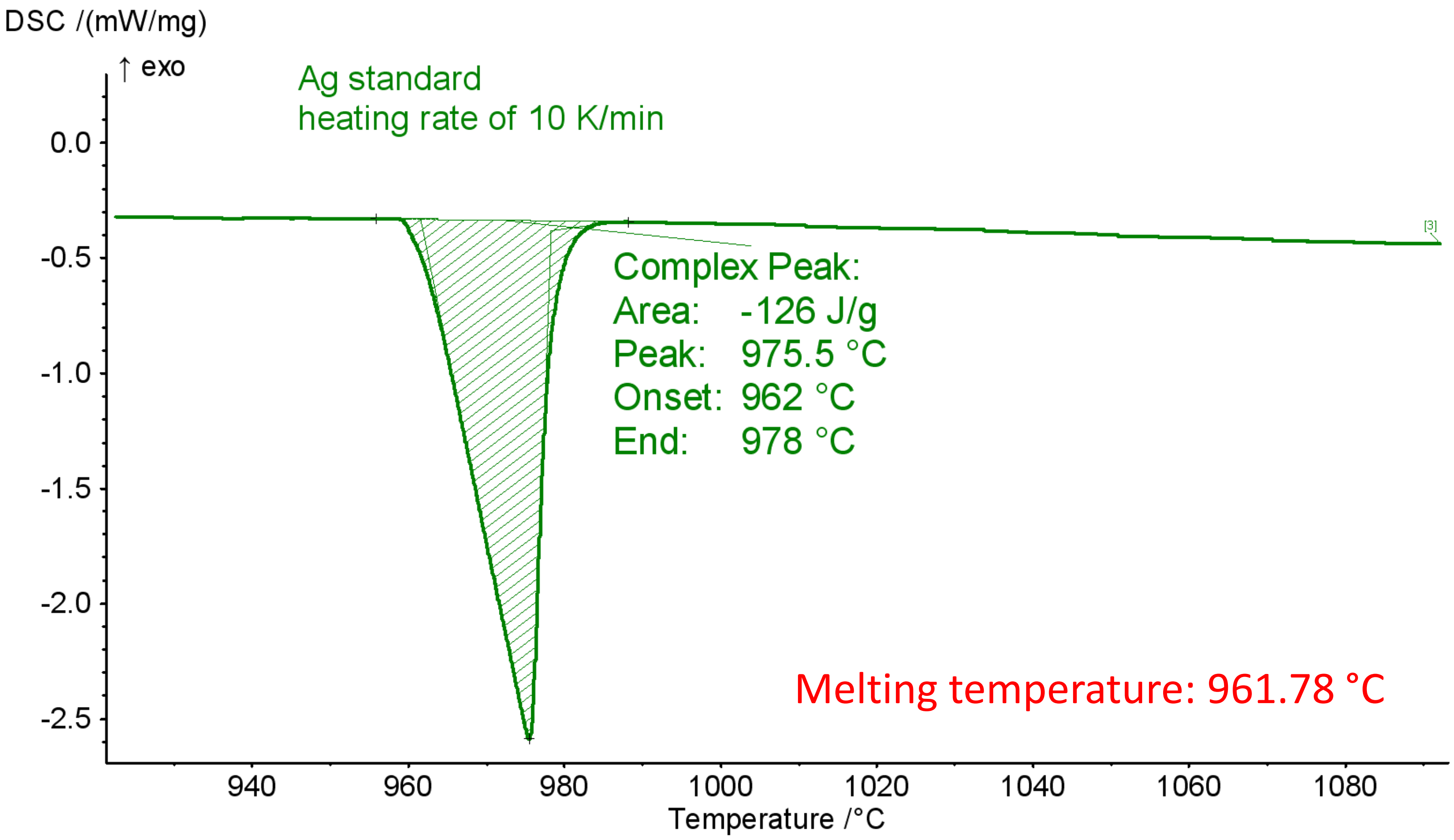
Onset temperature, T_{onset}: extrapolated start temperature of a process.

Endset temperature, T_{endset}: extrapolated temperature where the process ends.

Peak temperature, T_{peak}: the temperature of the highest/lowest reaction rate.

DTA responses to melting and freezing of a pure material under ideal conditions. a-onset temperatures (taken here as equal to the melting point, TM), b-peak signals, c-peak temperatures.

Curve analysis



Complex Peak:
Area: -126 J/g
Peak: 975.5 °C
Onset: 962 °C
End: 978 °C

Melting temperature: 961.78 °C

Application of the DTA and DSC technique

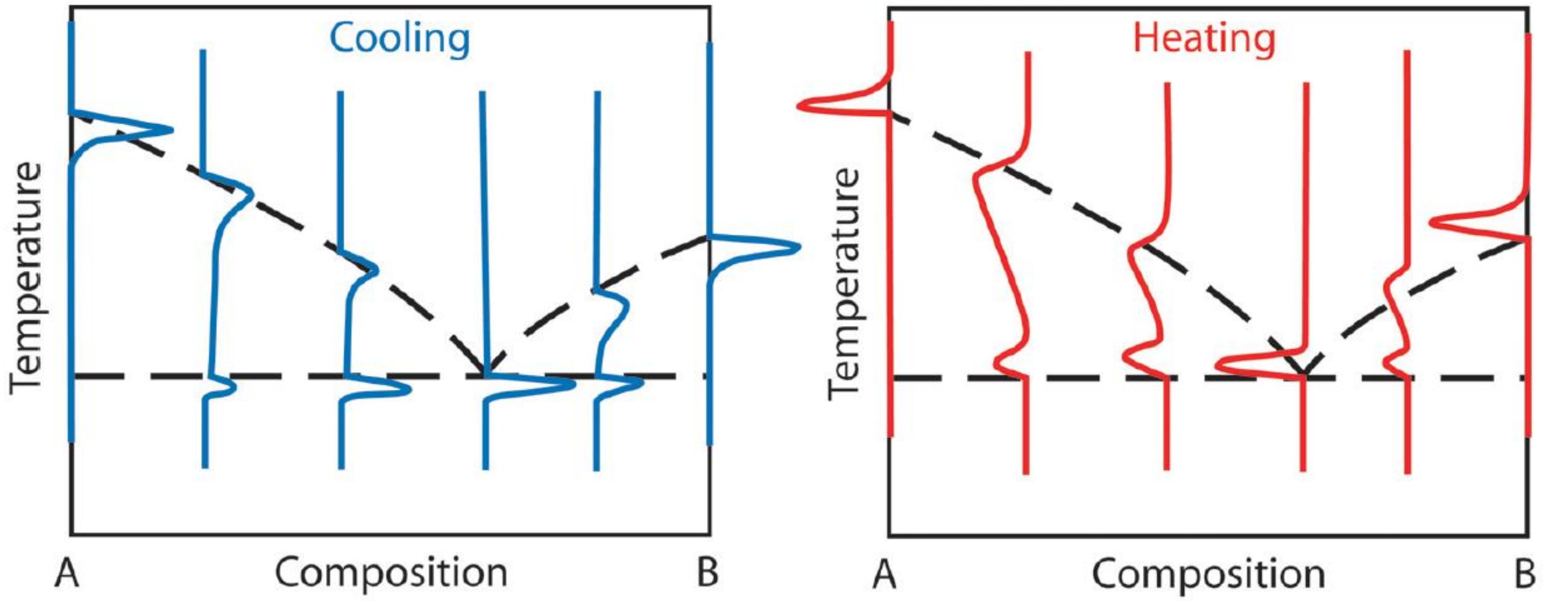


Figure 3.1. Schematic DTA response on coooling and heating of pure A and B and for other alloys superimposed on a simple eutectic phase diagram.

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