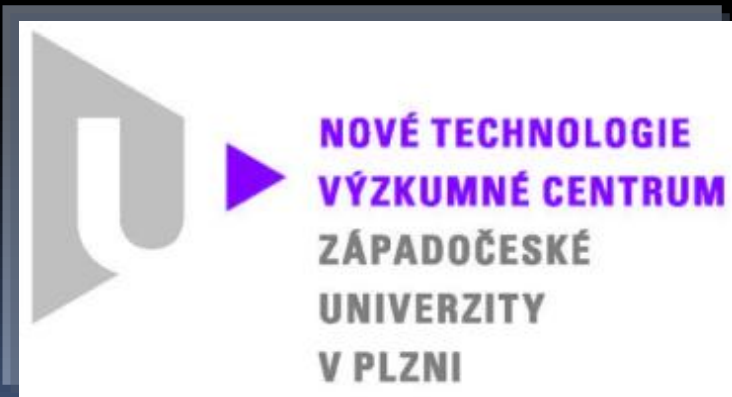


známe co měříme a vlastně
Víme co je teplota ?

Jaroslav Šesták

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Region, West Bohemian University, Universitni 8, CZ-
30114 Plzeň;

E-mail: sestak@fzu.cz



Kalsem 2018
Kutná hora

Санкт Петербург, Сентябрь 2013
St Petersburg , September 2013

with
← Igor Archangelski
and Jurij Metlin ↓



Dedicated to Pavel Holba
1940 - 2016

Holba last conference
CEEC Ljubljana 2015



NTC - With Broněk Foller

Pavel Holba received thermodynamic award
at CEEC-TACV conference,
Ljubljana, August 2015



Udělení nejvyšší ruské medaile Kurnakova za termodynamiku.

In memoriam RCTAC konference, St Pterburg, září 2016

Курнаков Н. С. 1860-1941 - Соединение и химический индивидъ



1918-34 - основатель и первый директор Института физико-химического анализа АН СССР

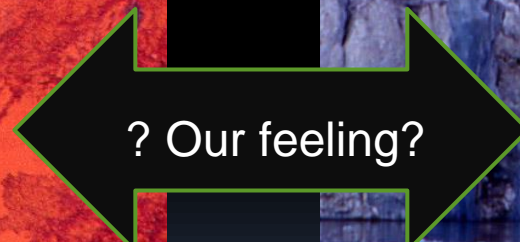
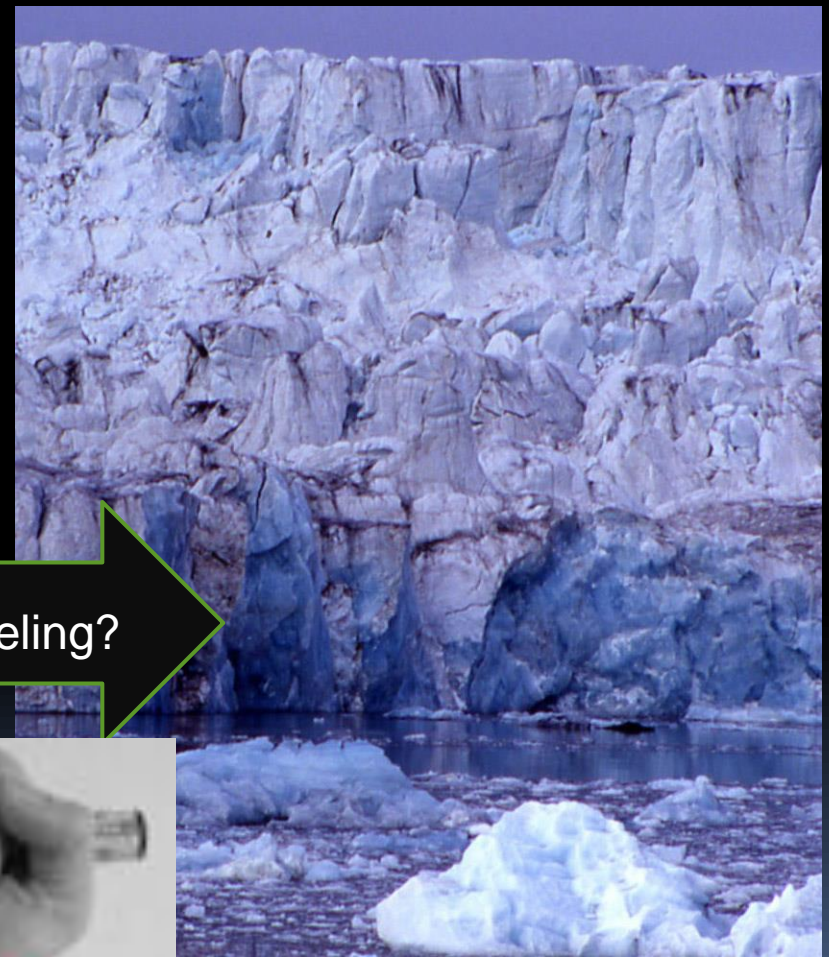
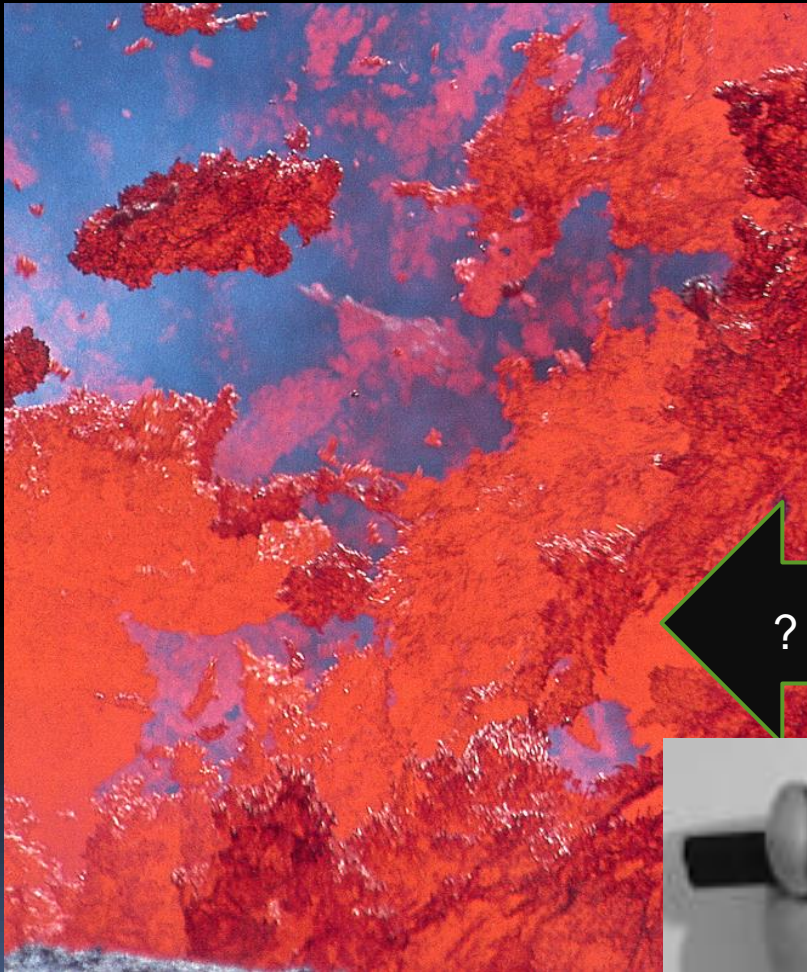
1925 - первое издание книги Введение в физико-химический анализ (2.; в 1928 г., 3. в 1935 г., 4. в 1940 г.- Изд АН СССР М.-Л. 562 стр.)

1937-41 - заведующий кафедрой неорганической химии МГУ

Tepłota vs. naše cíťění ?

heat = fire

cold = ice



Wood-worm

Holding a bar of ...

Metal- cold

Co měříme? Jak to měříme? Kde to měříme?
Vždycky něco naměříme !!



Velká vzdálenost



Velká rychlost




Logika versus fyzika/matematika

Co když ale budeme pozorovat chování teploty z jedoucího vlaku

Makroskopický extrém

Relativistická transformace


$$T = T_0 \sqrt{1 - v^2/c^2} \quad \text{K. v. Mosengeil (1907)}$$

$$T = T_0 / \sqrt{1 - v^2/c^2} \quad \text{H. Ott (1963)}$$


$$\mathbf{T} = \mathbf{T}_0 \quad \text{P. T. Landsberg (1966)}$$

⇒ Dlouhodobá kontraverze – problém relativistické fyziky

⇒ **Naše řešení**

$$\Rightarrow \mathbf{k} = \mathbf{k}_0 \sqrt{1 - v^2/c^2}, \quad \mathbf{R} = \mathbf{R}_0 \sqrt{1 - v^2/c^2}$$

J.J. Mareš, J. Šesták, V. Špička, P. Hubík, J. Krištofik, *Temperature Transformation and Mosengeil-Ott's Antinomy*. Physica E 42 (2010) 484

TEPLO, TEPLOTA, TEPLOZPYT



Temperature Heat
Temperatur Wärme
Température chaleur

Teplota **teplo**
Temperatura ciepło
Температура тепло

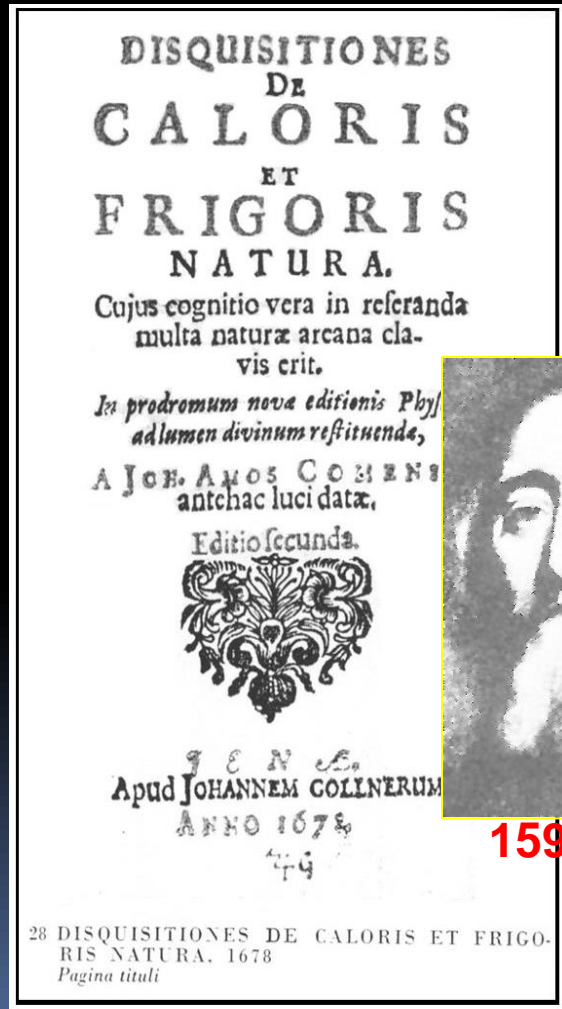
Θερμοκρασία Θερμότητα

Teplo – teplozpyt ↔ calorimetry

Kabaret
Majora
Kopřivy:
**Mrazospytem
k teplozpytu**



J.A. Komenský Heat: calor, fervor a ardor
Cold: frigus, algor and ??
Not yet distinguishing temperature



1592-1670

„ „Abychom účinky tepla a zimy spatřili světle, sluší se vzíti předmět viditelný i sluší se počítrovati změny jeho, když se ohřeje i když se zase ochladí, aby se očitě ukázalo, co teplo a zima dělají smyslům pochopitelné“

“ introduced „caloric“

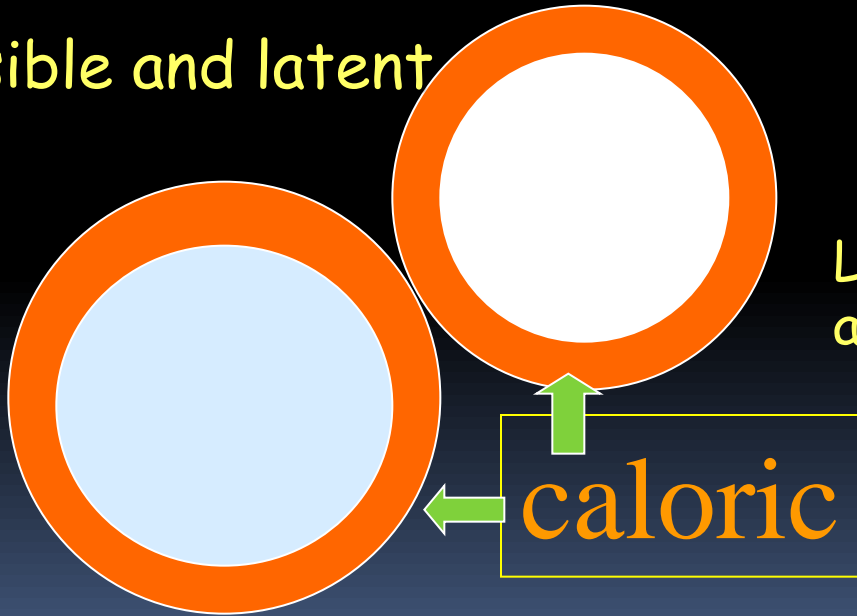
Reneissance :

phlogiston-fuel- palivina
caloricum-medium-teplík

▪ Becher, Stahl → phlogistom (terra pinquis)

Metal = CALX + phlogiston

Sensible and latent
heat



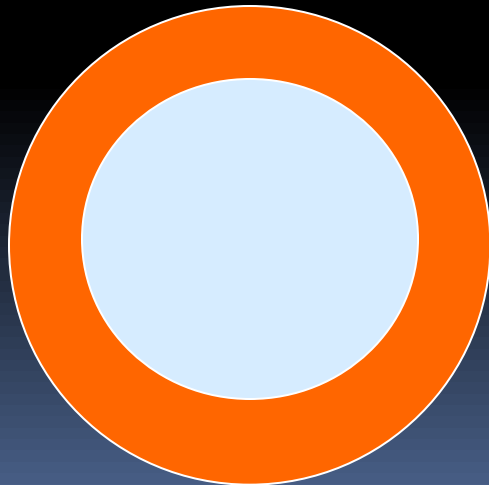
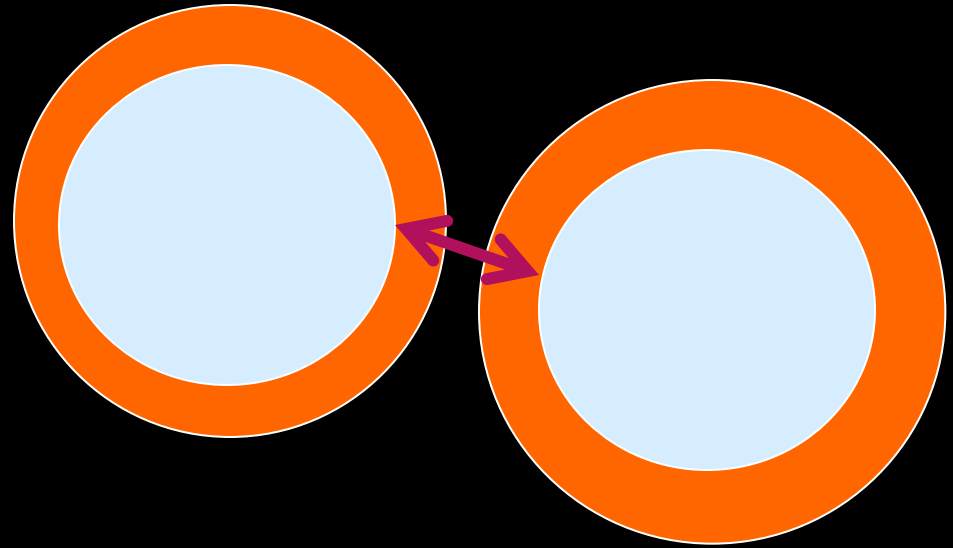
Logarithmic dependence between
amount (quantity) and intensity

← **Black, Irving, Sheele**
Pristley, Cavendish

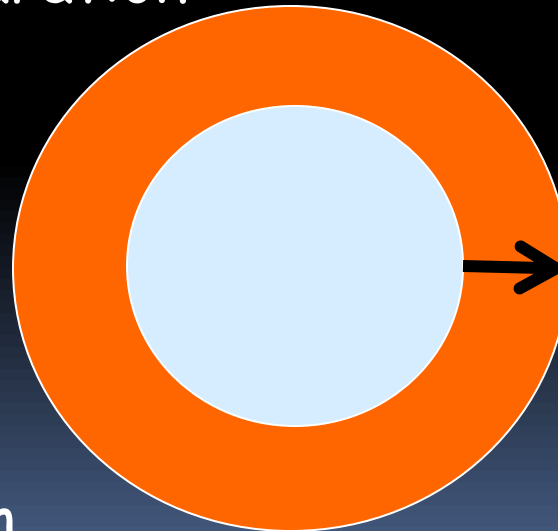
In order to stay away from a total gravitational collision, which would produce a single homogeneous mass, the opposing force was considered to be the '*self-repulsive caloric*'. Such an early '*fluid*' hypothesis became important in the formulation of modern laws and was common to the way of thinking of early Greeks (*Archimedes*).



phase separation

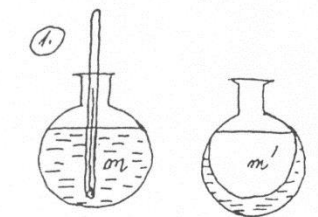


dilatation



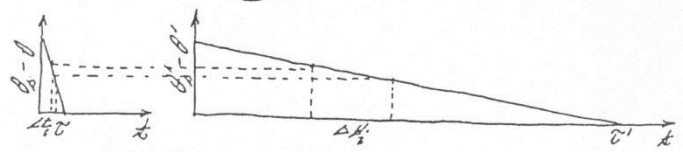
Distinguishing specific heat, latent heat and temperature: launching thermometry and calorimetry

and calorimetry



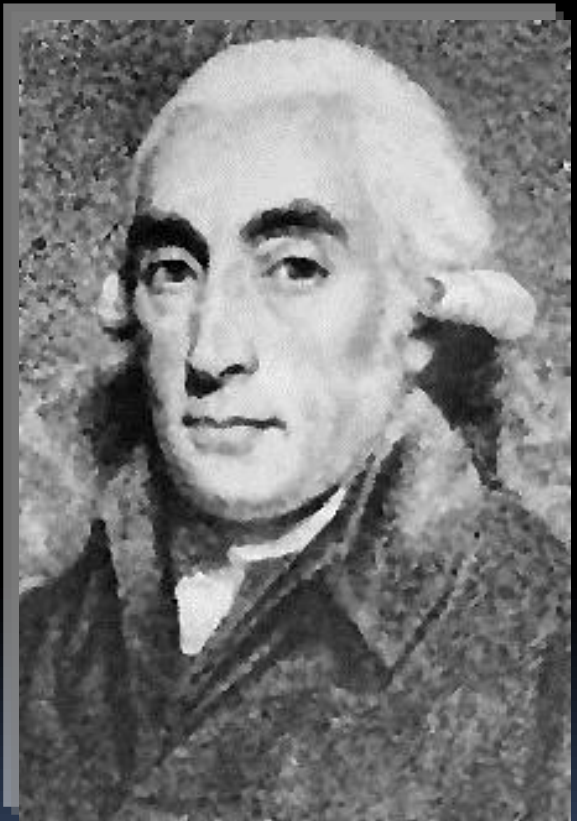
$1 \text{ ounce} = 8 \text{ drachms} \approx 28.8 \text{ g}$
 $1 \text{ drachm} = 3 \text{ scruples} \approx 3.6 \text{ g}$
 $1 \text{ scruple} = 20 \text{ grains} \approx 1.28 \text{ g}$
 $1 \text{ grain} \approx 0.064 \text{ g}$

$\lambda_{\text{ice}} = 334.1 \text{ J} \cdot \text{g}^{-1} \rightarrow \Lambda = 79.8^\circ\text{C} \rightarrow 143.6^\circ\text{F}$



$m = m' = 6 \text{ ounces}$
 $\theta_s = \theta'_s = 47^\circ\text{F}; \theta_0 = \theta'_0 = 33^\circ\text{F}; \theta_e = \theta'_e = 40^\circ\text{F}; (\theta_e - \theta_0)_i = \Delta\theta_{\text{exp}} = 7^\circ\text{F}$
 $\tau = 0.5 \text{ h}; \tau' = 10.5 \text{ h}; \tau/\tau = 21; \Delta\theta'_i = (\tau'/\tau) \Delta\theta_i$
 $\delta\theta_i = k \cdot (\theta_s - \theta_0) \cdot \Delta t_i; \delta\theta'_i = k (\theta'_s - \theta'_0) \Delta t'_i = (\tau'/\tau) \cdot k \cdot (\theta_s - \theta_0) \Delta t_i$
 $\Delta\theta'_{\text{int}} = \frac{\tau'}{\tau} [k \sum (\theta_s - \theta_0) \cdot \Delta t_i] = \frac{\tau'}{\tau} \cdot \Delta\theta_{\text{exp}} = 21 \cdot 7^\circ\text{F} = 147^\circ\text{F}$
 $\Lambda = 147^\circ\text{F} - 7^\circ\text{F} = 140^\circ\text{F} (\rightarrow 77.8^\circ\text{C} \rightarrow 325.7 \text{ J} \cdot \text{g}^{-1})$

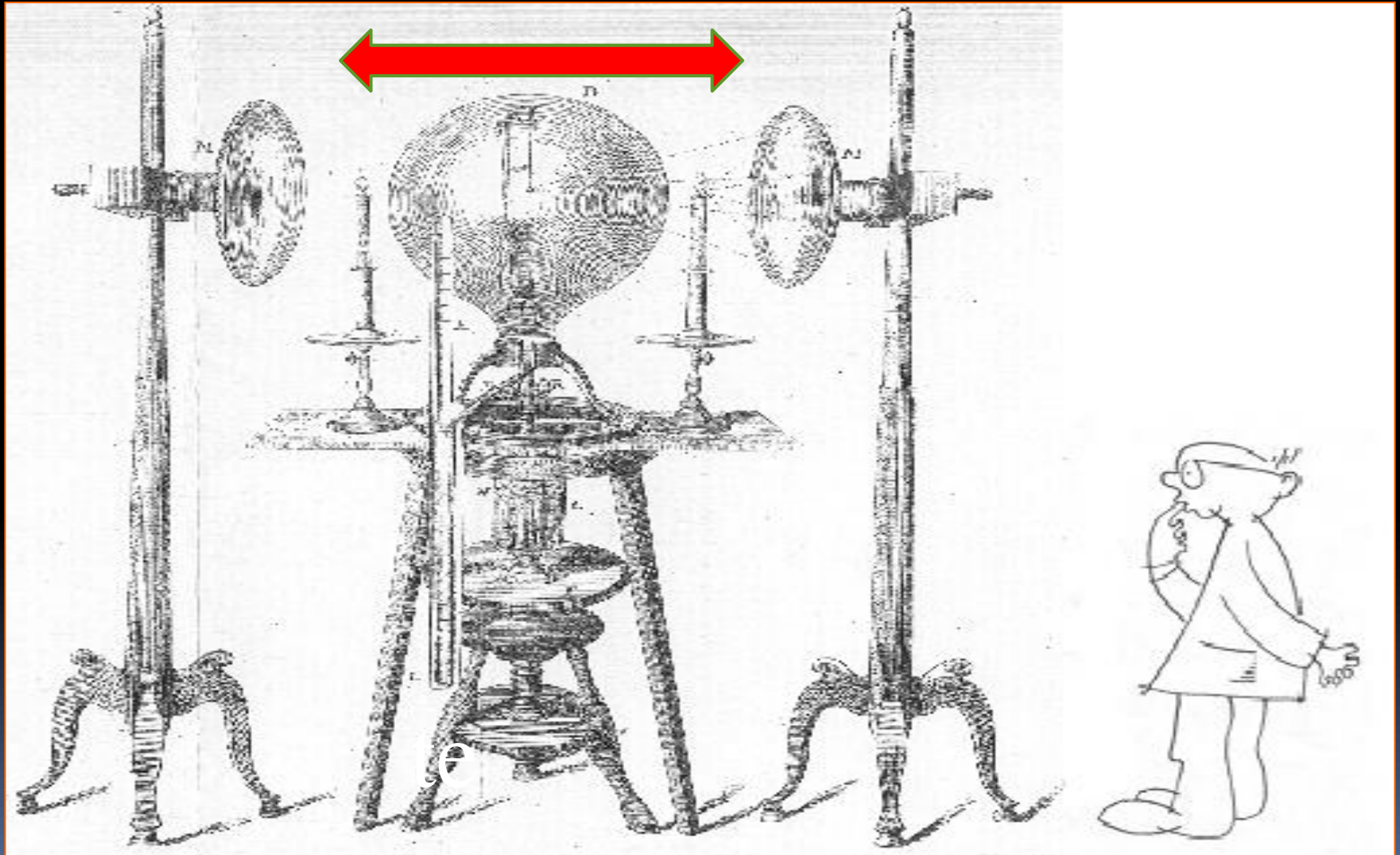
$m(\text{H}_2\text{O}, s) = 119 \text{ h.d. (half drachm)}$
 $m(\text{H}_2\text{O}, l) = 135 \text{ h.d.}$
 $m(\text{H}_2\text{O}, s, l) = 254 \text{ h.d.}$
 $m(\text{gl.}) = 16 \text{ h.d.} \Rightarrow m(\text{H}_2\text{O}, l, \text{gl.}) = 8 \text{ h.d.}$
 $\theta(\text{H}_2\text{O}, s) = 32^\circ\text{F}; \theta(\text{H}_2\text{O}, l) = \theta(\text{gl.}) = 190^\circ\text{F}; \theta(\text{H}_2\text{O}, l, s, \text{gl.}) = 53^\circ\text{F}$
 $c = c(\text{H}_2\text{O}, l, \text{h.d.}, \Delta\theta = 1^\circ\text{F}); \lambda = \lambda(\text{H}_2\text{O}, s \rightarrow l, \text{h.d.})$
 $[m(\text{H}_2\text{O}, l) + m(\text{H}_2\text{O}, l, \text{gl.})] \cdot c \cdot [\theta(\text{H}_2\text{O}, l) - \theta(\text{H}_2\text{O}, s, l, \text{gl.})] =$
 $= m(\text{H}_2\text{O}, s) \cdot \lambda + m(\text{H}_2\text{O}, s) \cdot c \cdot [\theta(\text{H}_2\text{O}, l, s, \text{gl.}) - \theta(\text{H}_2\text{O}, s)]$
 $(135 + 8) \text{ h.d.} \cdot c \cdot (190 - 53)^\circ\text{F} = 119 \text{ h.d.} \cdot \lambda + 119 \text{ h.d.} \cdot c \cdot (53 - 32)^\circ\text{F}$
 \downarrow
 $\frac{\lambda}{c} \cdot \Lambda = \frac{143 \text{ h.d.}}{119 \text{ h.d.}} \cdot 137^\circ\text{F} - \frac{119 \text{ h.d.}}{119 \text{ h.d.}} \cdot 21^\circ\text{F} = 143.6^\circ\text{F}$



J. Black (1728-1799)
J. Irvine (1733-1791)

Poincaré 1790

Particles of **HEAT** and **COLD**



Heat as an element

ELEMENTS *Education of Chemistry* CHEMISTRY,

IN A
NEW SYSTEMATIC ORDER,
CONTAINING ALL THE
MODERN DISCOVERIES.

ILLUSTRATED WITH THIRTEEN COPPERPLATES.

BY MR LAVOISIER,

Member of the Academy of Sciences, Royal Society of Medicine, and Agricultural Society of Paris, of the Royal Society of London, and Philosophical Societies of Orleans, Bologna, Basil, Philadelphia, Haerlem, Manchester, &c. &c.

TRANSLATED FROM THE FRENCH,

BY ROBERT KERR, F.R. & A.S.S.E.

Member of the Royal College of Surgeons, and Surgeon of the Hospital of Edinburgh.

EDINBURGH:
WILLIAM CREECH, AND SOLD
G. G. AND J. J. ROBINSONS.

MDCCCXC.



Ivo Proks

„CELOK JE JEDNODUCHŠÍ AKO JEHO ČASTI“

Vybrané kapitoly z histórie exaktných prírodných vied

VEDA
VYDAVATELSTVO
SLOVENSKEJ
AKADÉMIE
VIED

ELEMENTS TABLE OF SIMPLE SUBSTANCES.

Simple Substances belonging to all the kingdoms of nature, which may be considered as the elements of bodies.

Light	New Names.	Correspondent old Names.
		Light.
		Heat.
Caloric		Principle or element of heat.
		Fire. Igneous fluid.
		Matter of fire and of heat.
		Dephlogisticated air.
Oxygen		Empyreal air.
		Vital air, or
		Base of vital air.
Acce		Phlogisticated air or gas.
		Mephitic, or its base.
Hydrogen		Inflammable air or gas,
		or the base of inflammable air.

Oxydable and Acidifiable simple Substances not Metallic.

New Names.	Correspondent old names.
Sulphur	The same names.
Phosphorus	
Carboc.	
Mercuric radical	
Fluoric radical	Still unknown.
Baroc radical	

Oxydable and Acidifiable simple Metallic Bodies.

New Names.	Correspondent Old Names.
Antimony	Antimony.
Arsenic	Arsenic.
Bismuth	Bismuth.
Cobalt	Cobalt.
Copper	Copper.
Gold	Gold.
Iron	Iron.
Lead	Lead.
Manganese	Manganese.
Mercury	Mercury.
Molybdena	Molybdena.
Nickel	Nickel.
Platina	Platina.
Silver	Silver.
Tin	Tin.
Tungstain	Tungstain.
Zinc	Zinc.

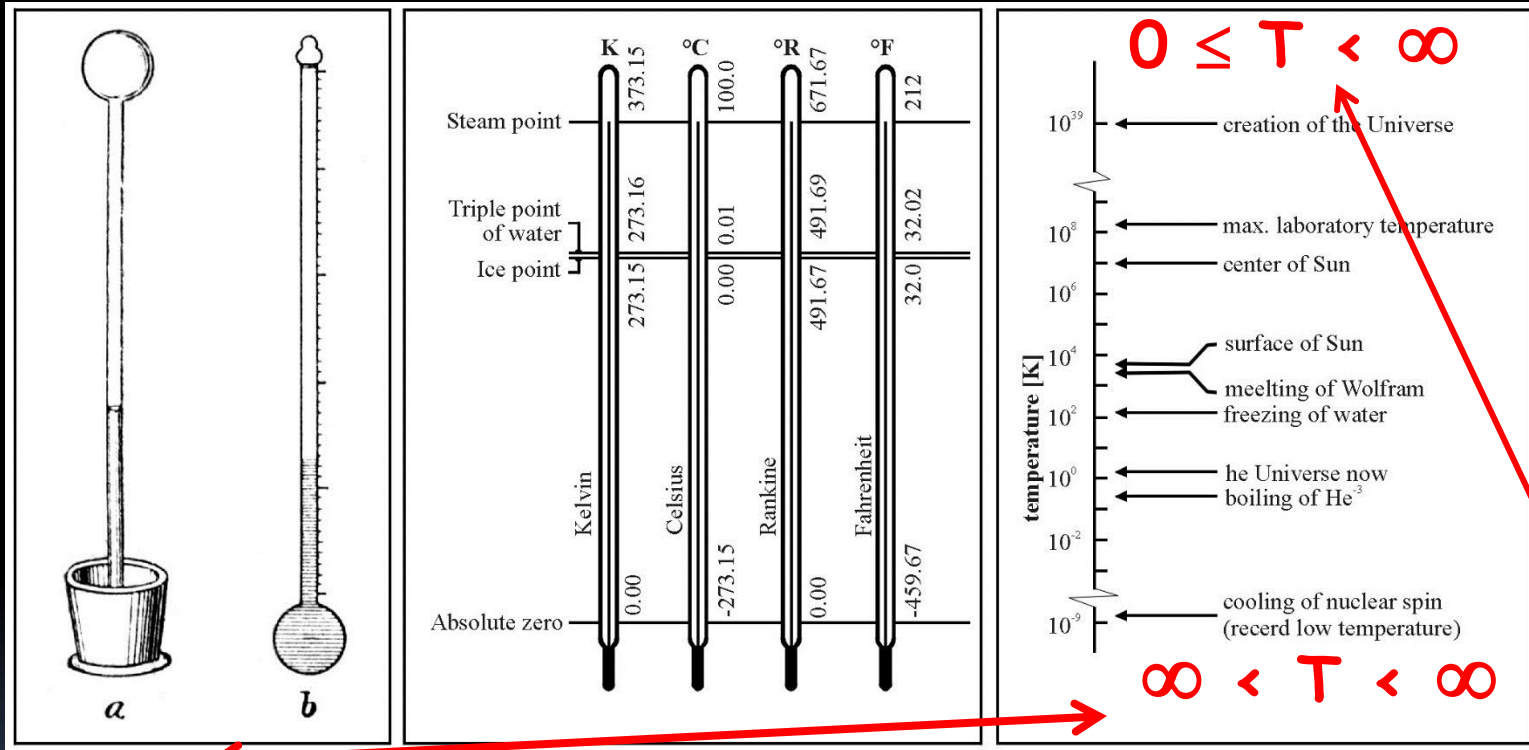
Salifiable simple Earthy Substances.

New Names.	Correspondent old Names.
Lime	Chalk, calcareous earth.
	Quicklime.
Magnesia	Magnesia, base of Epsom salt.
	Calcined or caustic magnesia.
Barytes	Barytes, or heavy earth.
Argill	Clay, earth of alum.
Silex	Siliceous or vitrifiable earth.

Temperature scale & calibration



Čím horší pivo, tím dříve zmrzne



Newton ($T=12 \{2^{x-1}\}, 0-34$), Amontons ($V \rightarrow 0, T \rightarrow 0$)
 \Rightarrow Kelvin, Römer, Fahrenheit, 32-212), Celsius (100-0
 \Rightarrow Linné 0-100), Thomson ($Th = c1 \ln T + c2, To \rightarrow \infty$)

Jan Amos Comenius: What is what in TA ?

"to observe clearly the effect of heat and cold, a visible object should be subjected to heating and subsequent cooling, the sensible changes made by heat and cold will then be visible to the eye" **Seventeen Century**

Thermal analysis is a branch of materials science where the properties of materials are studied as they change with temperature. Several methods are commonly used - these are distinguished from one another by the property which is measured

Wikipedia definition

Temperature T
(heat q)
Thermal analysis
T vs T or T vs time

macro ??

Universe, Earth climate, weather

Universe	10^6 light years
planet	km
← man	m (sec)
molecule	nm
electron	10^{-16} m



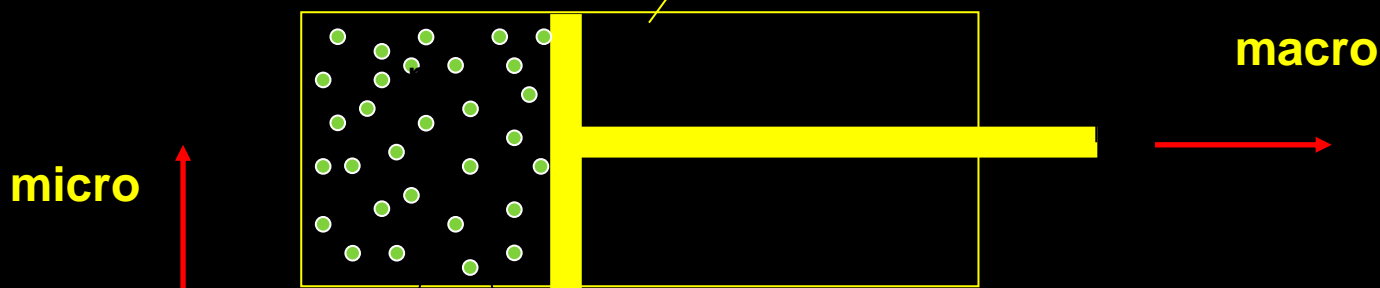
Chemical and quantum processes

micro ??

Thermodynamic laws

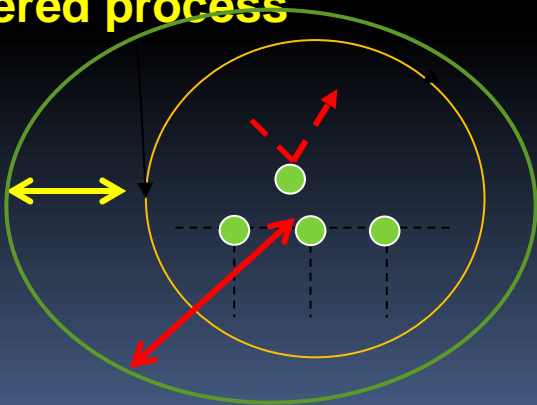
difference between „Order“ and „Chaos“

Temperature and heat/entropy

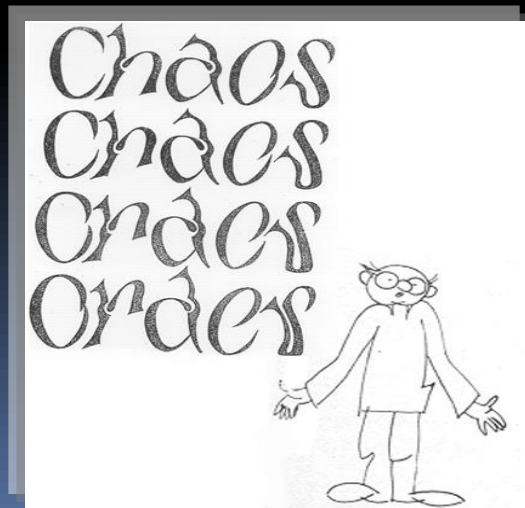


we cannot use energy arbitrarily because of entropical limits

$$\Delta U/\Delta V = P \Rightarrow \text{ordered process}$$



$$\Delta U/\Delta S = T \Rightarrow \text{chaotic process}$$



Similarity of Newton's law of gravitation

$$F = m a$$

ensue many other principles

Law of heat transfer (Fourier)	$\mathbf{q} = \lambda \nabla T$
Law of diffusion (Fick)	$\mathbf{J} = D \nabla c$
Law of electric flow (Ohm)	$\mathbf{I} = r \nabla u$
Law of thermal inertia	$Y_i = C_p d^2 T / dT^2$



Fluid-like
flow of
'caloricum'



As well as surface tension, mobility in liquids,
(such as further Stokes', Newton's law) etc

?What is caloricum

In modern theories?

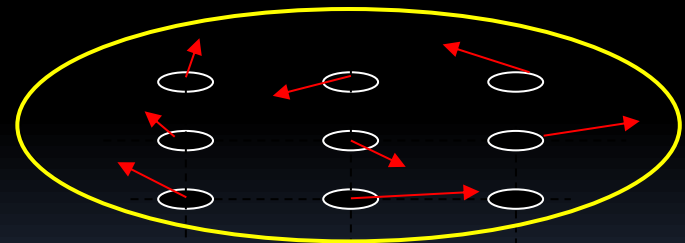
Fluid-like transfer

Pouring liquid and filling a bottle is not instantaneous but needs certain time



Inserting "heat" to the vibration and ordering modes is not immediate but needs explicit time

C_p



m

similarity



Any matter transport desires definite time lag



Heat sink within the sample thermal capacity

Gravity on a micro-level

Newton gave to us the deterministic description of our physical world whilst always aware that it could be a part of a superior universe (extending from the very small to the extremely large). He intuitively associated heat conduction with temperature gradients called '*gradus caloricum*' (whereupon gradient is derived from Greek '*gradus*' which means felicitous, congenial). *Newton* even tried to make some **quantitative observations by heating** one end of a metallic bar and observing heat propagation by detecting the progress of melting of various substances (wax) at different distances. It helped him to **formulate the law of cooling without knowing what heat actually was**. Let's remind heat flow q is dependent on temperatures T_h and T_c and heat capacities C :

$$q = K(T_h - T_c) = C_h (dT_h/dt) + C_c (dT_c/dt)$$

assuming C_c , C_h and $T_c = \text{const}$, we obtain

$$K(T_h - T_c) = - C_h (dT_h/dt) \Rightarrow K(T_h - T_c) dt + C_h dT_h = 0$$

$$(K / C_h) dT = d \ln K(T_h - T_c)$$

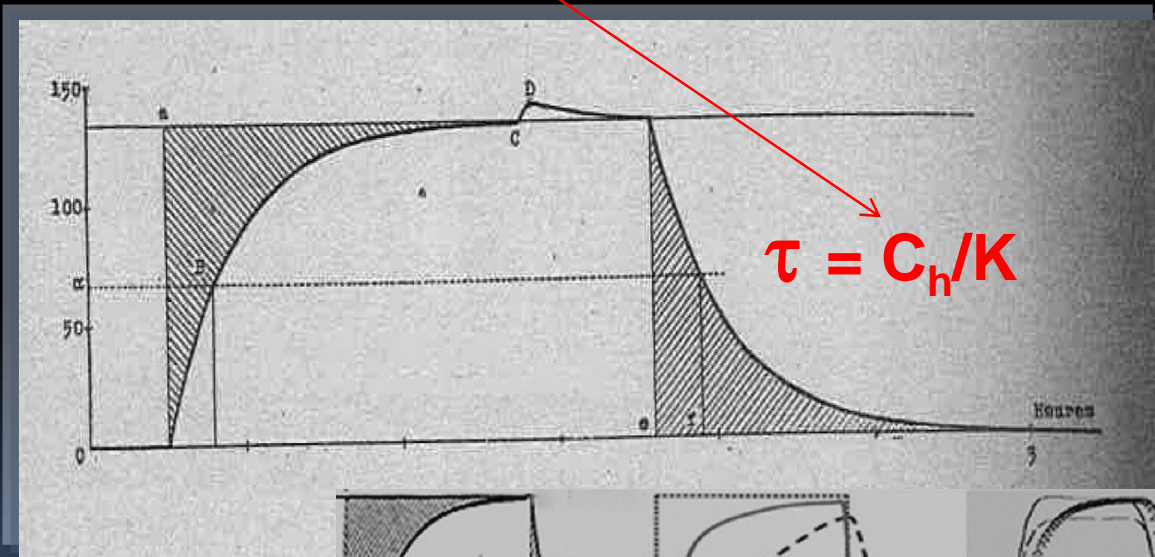


$$(T_h - T_c) = (T_{ho} - T_c) \exp (- (t - t_0)/\tau)$$

where T_{ho} is the *initial temperature* of hot body and

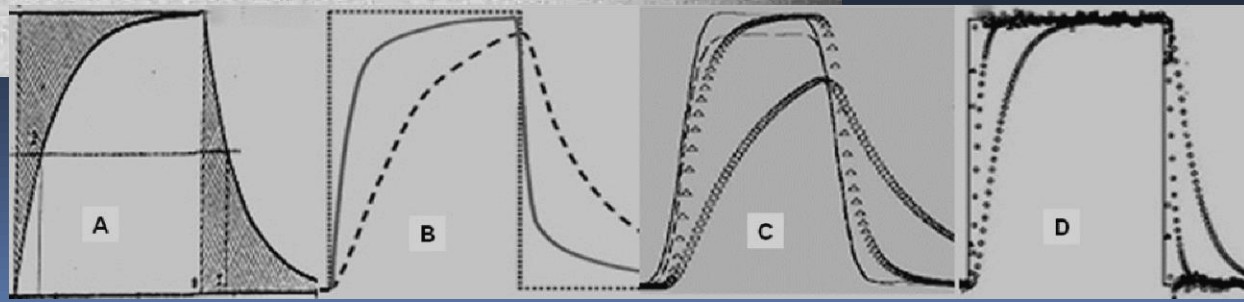
$\tau = C_h/K$ is called **time constant of cooling**.

Latter applied by Tian in his basic calorimetric equation



$$\tau = C_h/K$$

Present day \Downarrow

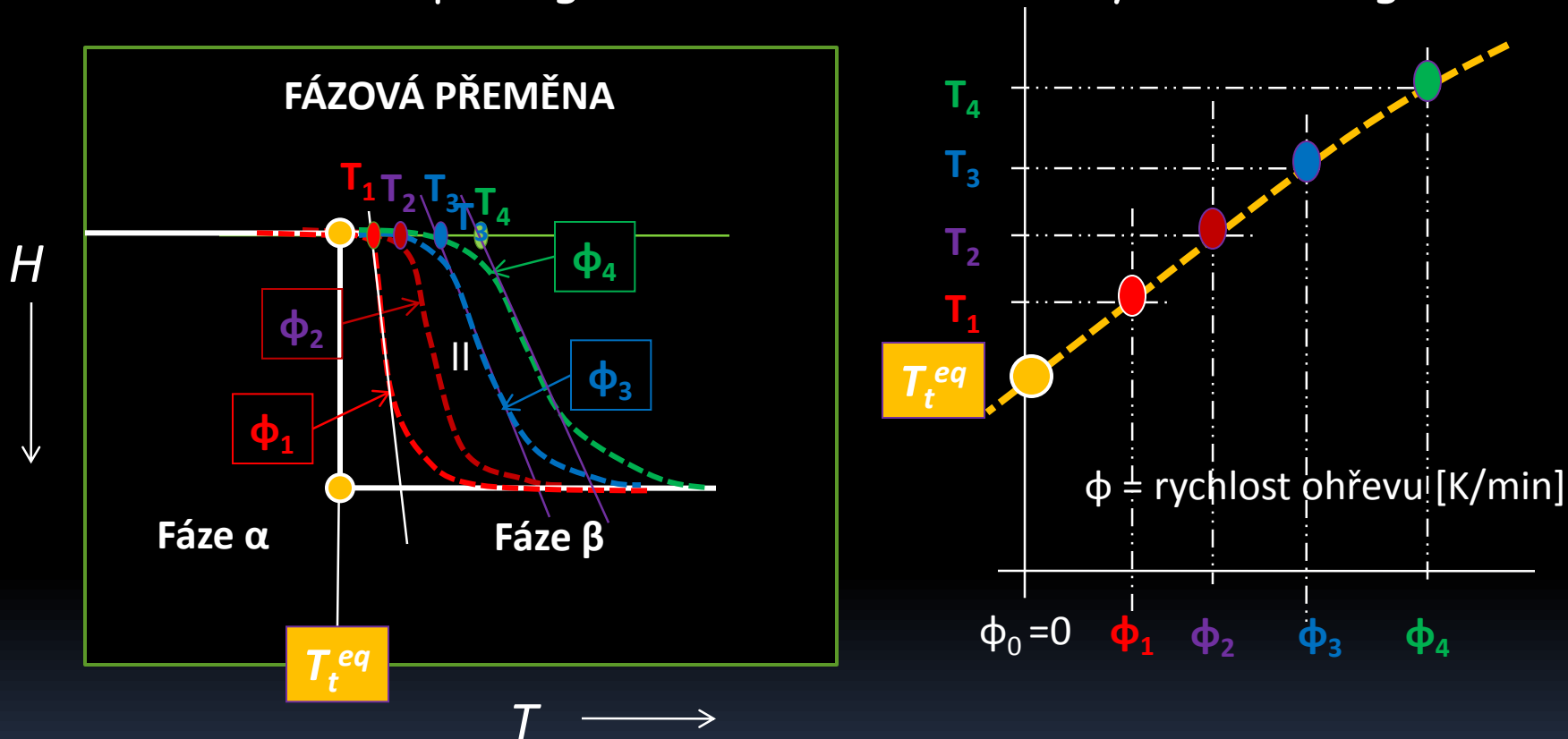


History 1933



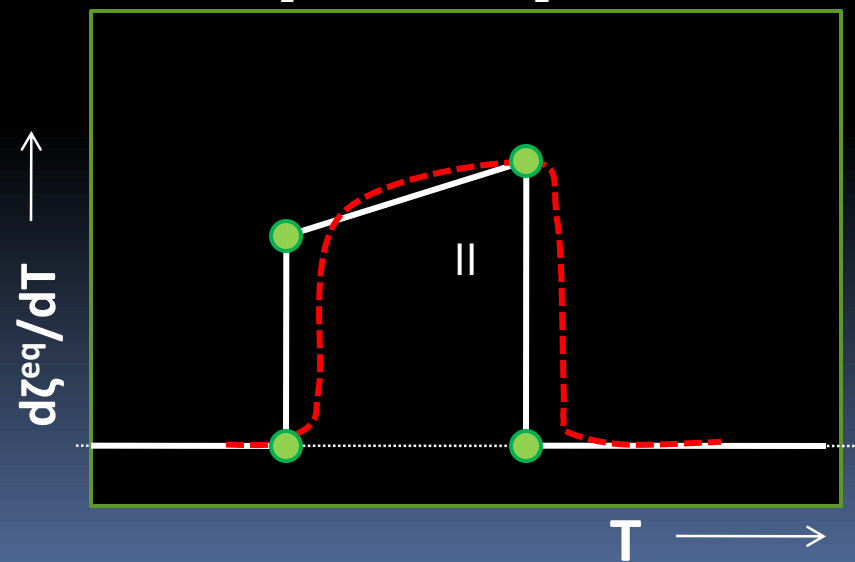
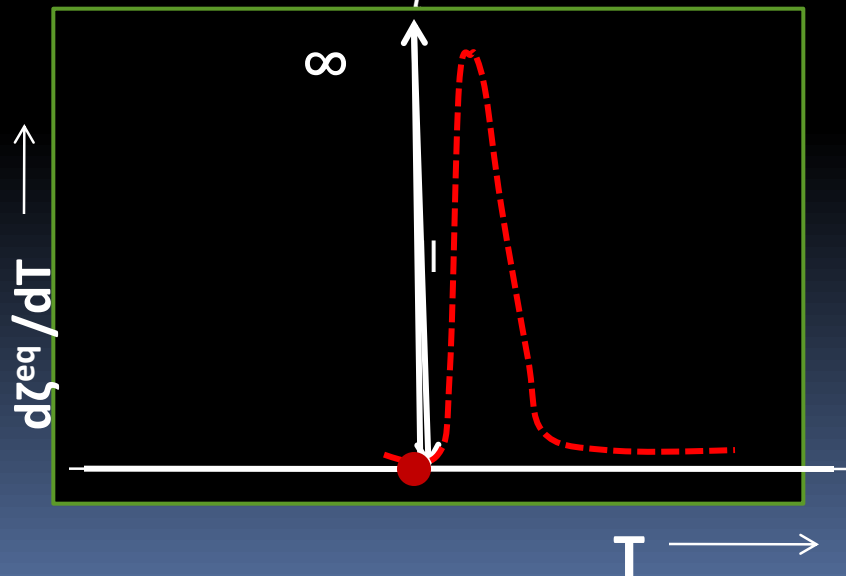
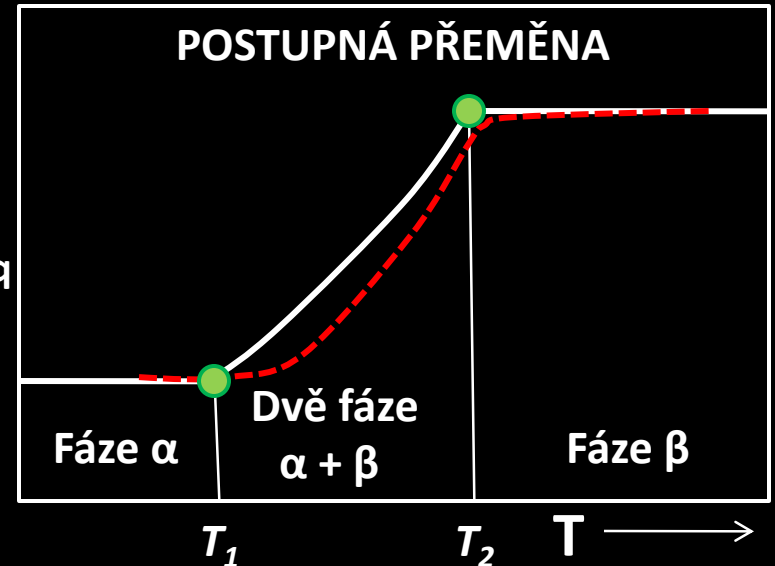
Rovnovážná teplota fázové přeměny: T_t^{eq}

Holba's life attempt to give kinetics its thermodynamic background



Holba P., Šesták J. (1972) Kinetics with regard to the equilibrium of processes studied by non-Isothermal techniques, Zeit. physik. Chem. N.F. 80: 1; and Holba P (2015) Ehrenfest equations for calorimetry and dilatometry. J Therm Anal Calorim. 120, 175-181.

Fázové přeměny a teplotní derivace entalpie



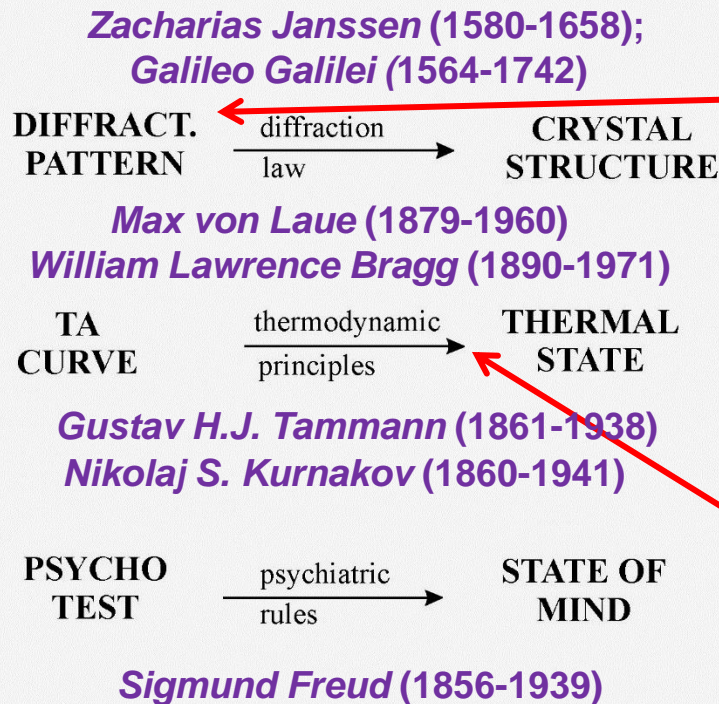
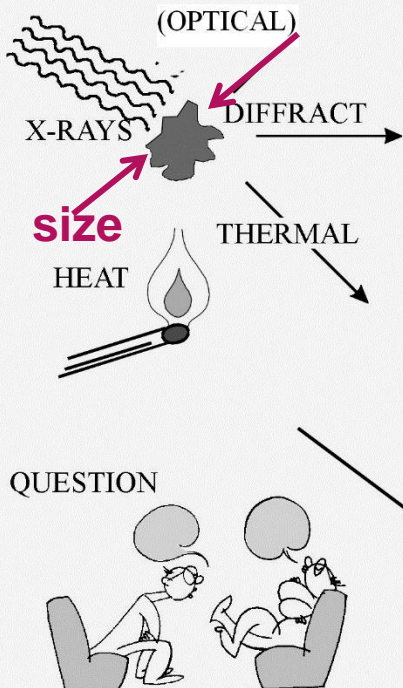
ANALYSIS analogy

SEARCH FOR INFORMATION

Information transducer

Type of analysis

Data treatment



*Zacharias Janssen (1580-1658);
Galileo Galilei (1564-1742)*

*Max von Laue (1879-1960)
William Lawrence Bragg (1890-1971)*

*Gustav H.J. Tammann (1861-1938)
Nikolaj S. Kurnakov (1860-1941)*

Sigmund Freud (1856-1939)

Instrumental interface

Evaluation procedure

optical ~ 600 nm
(set-up of crystals)

Nondestructive

X-ray ~ 0.5 nm
(ordering of atoms)

Destructive

Spectroscopic methods

Heat transfer methods

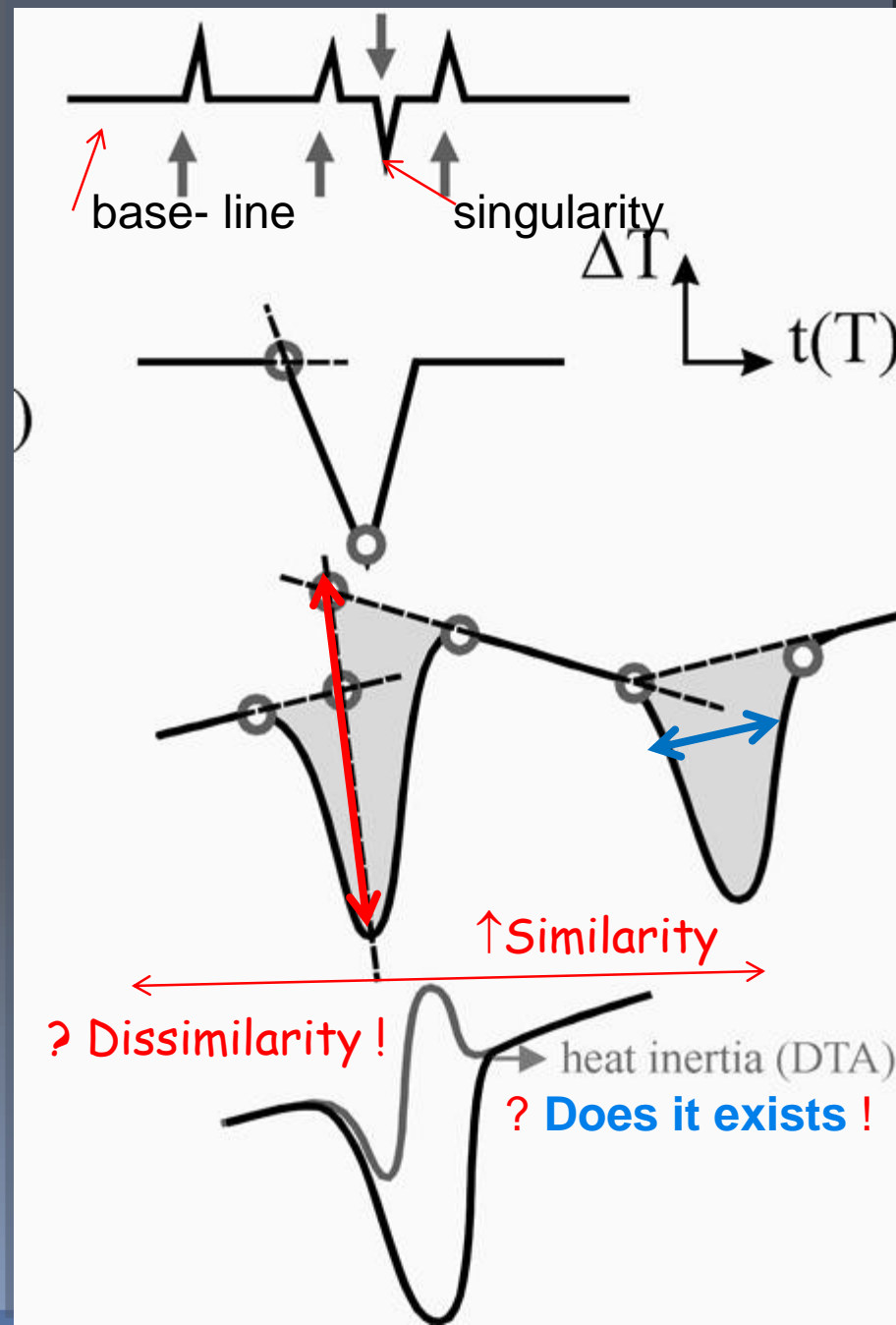
X-ray

Identity
"fingerprint"

Position
Symmetry
Quality

Quantity
Intensity
Area

Shape
Broadening
Crystal size



DTA

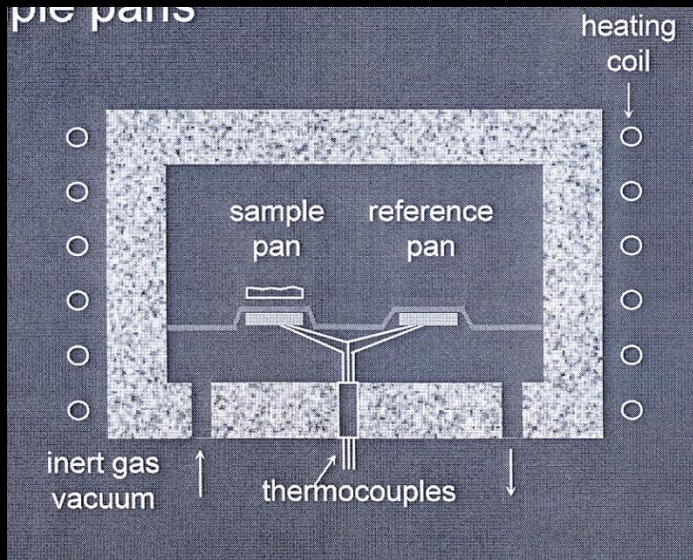
Identity
"fingerprint"

Position
Uniformity
Quality

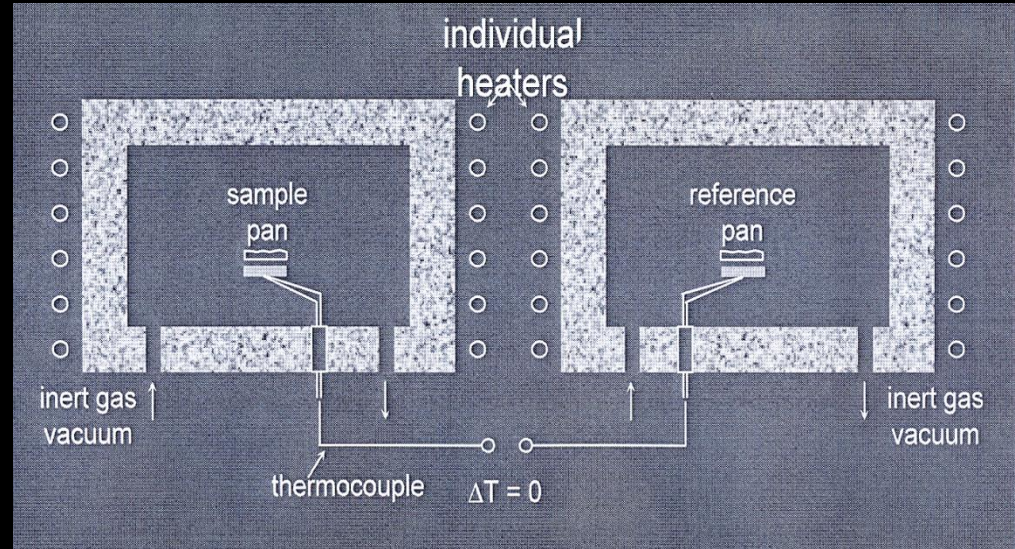
Quantity
Size
Area

Shape
Structure
Kinetics

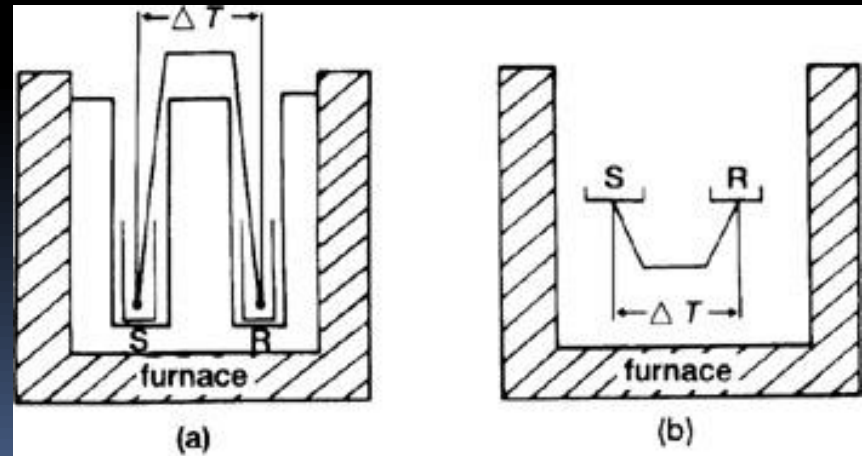
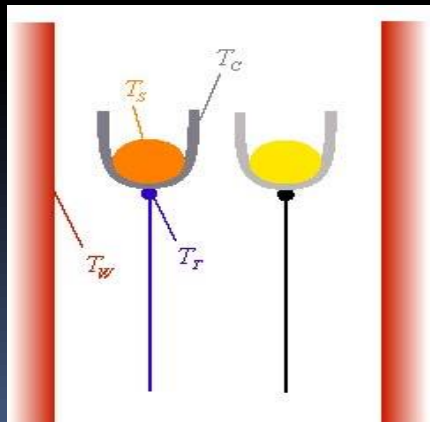
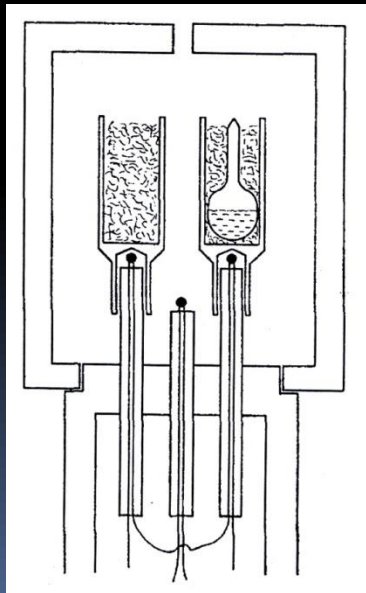
Heat-flux DSC



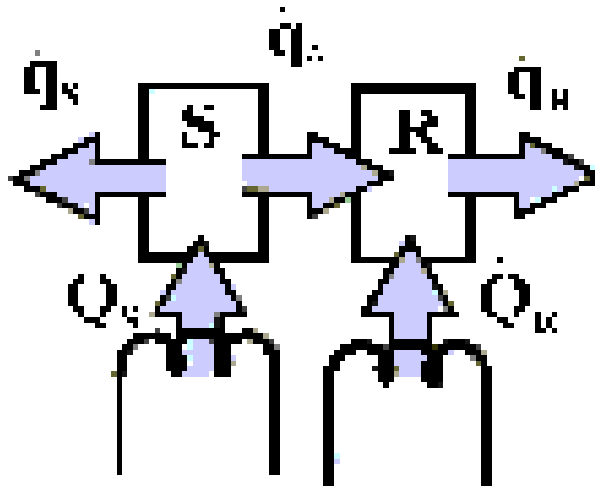
Compensation DSC



DTA



DTA equation



Enumerated for both the sample, s, and the reference, r,

DTA

$$q's = \Lambda s (Ts - Tj)$$

$$q'\Delta = \Lambda\Delta (Ts - Tr)$$

$$\Delta H's = q's + q'\Delta + Q's$$

$$\Delta T = [- \Delta HS \alpha' + (CpS - CpR)\phi + CpS \Delta T'] / \Lambda S$$

DSC

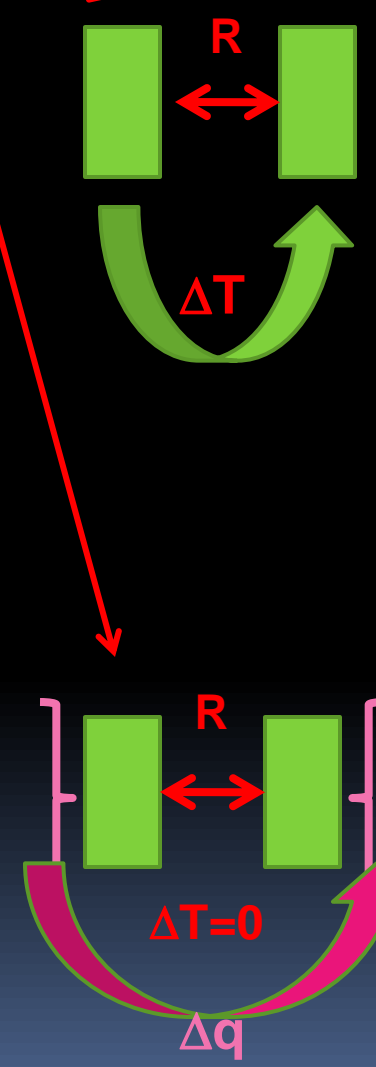
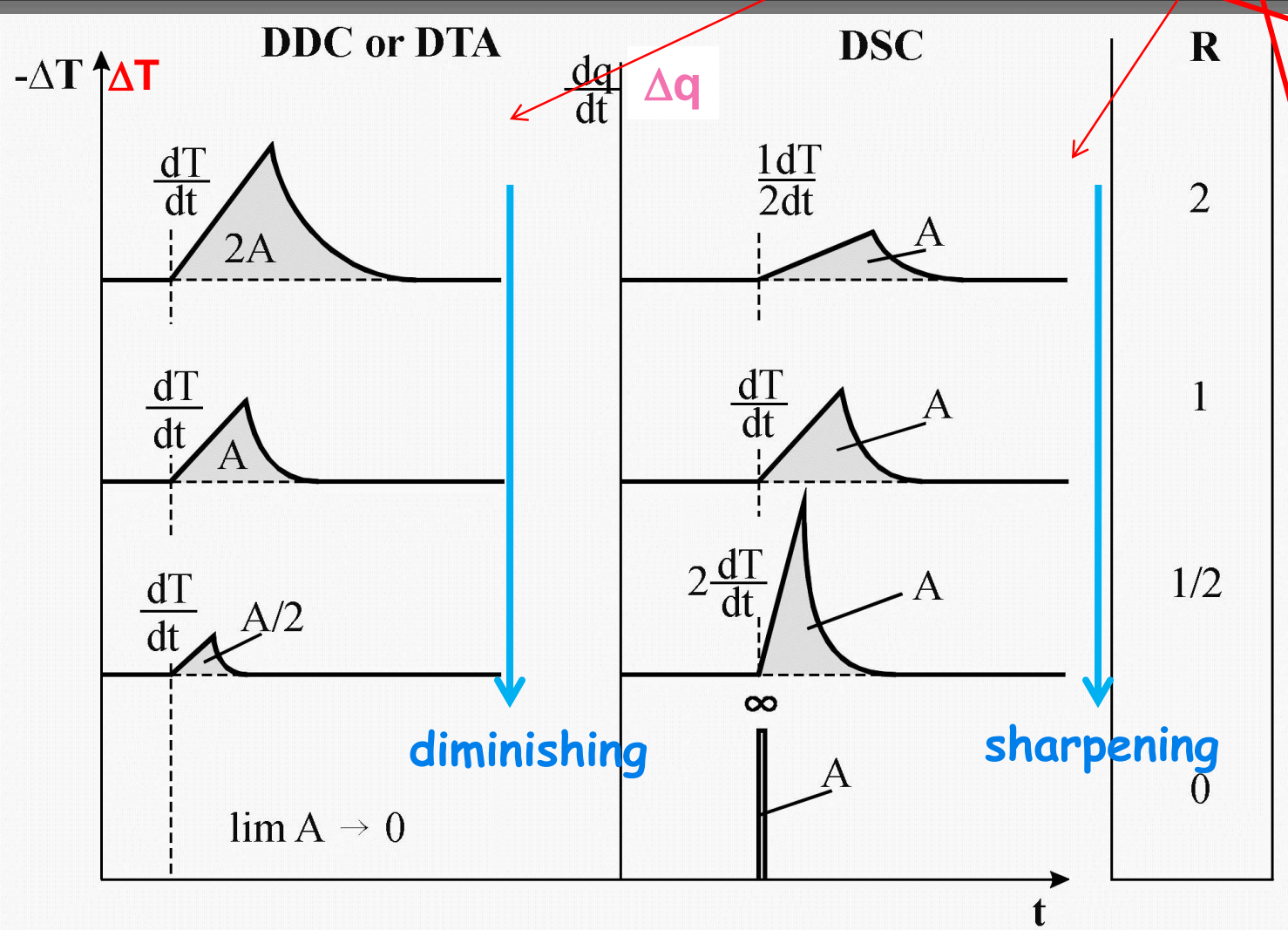
$$(Ts \cong Tr) \text{ and } \Delta T_{DTA} \approx 0$$

$$\Delta Q' = - \Delta Hs \alpha' + (Cps - Cpr)\phi + \Delta \Lambda (T - Tj)$$

Šesták J, Holba P (2013) Heat inertia and temperature gradient in the treatment of DTA peaks: Existing on every occasion of real measurements but until now omitted. J Thermal Anal Calorim 113: 1633-1643

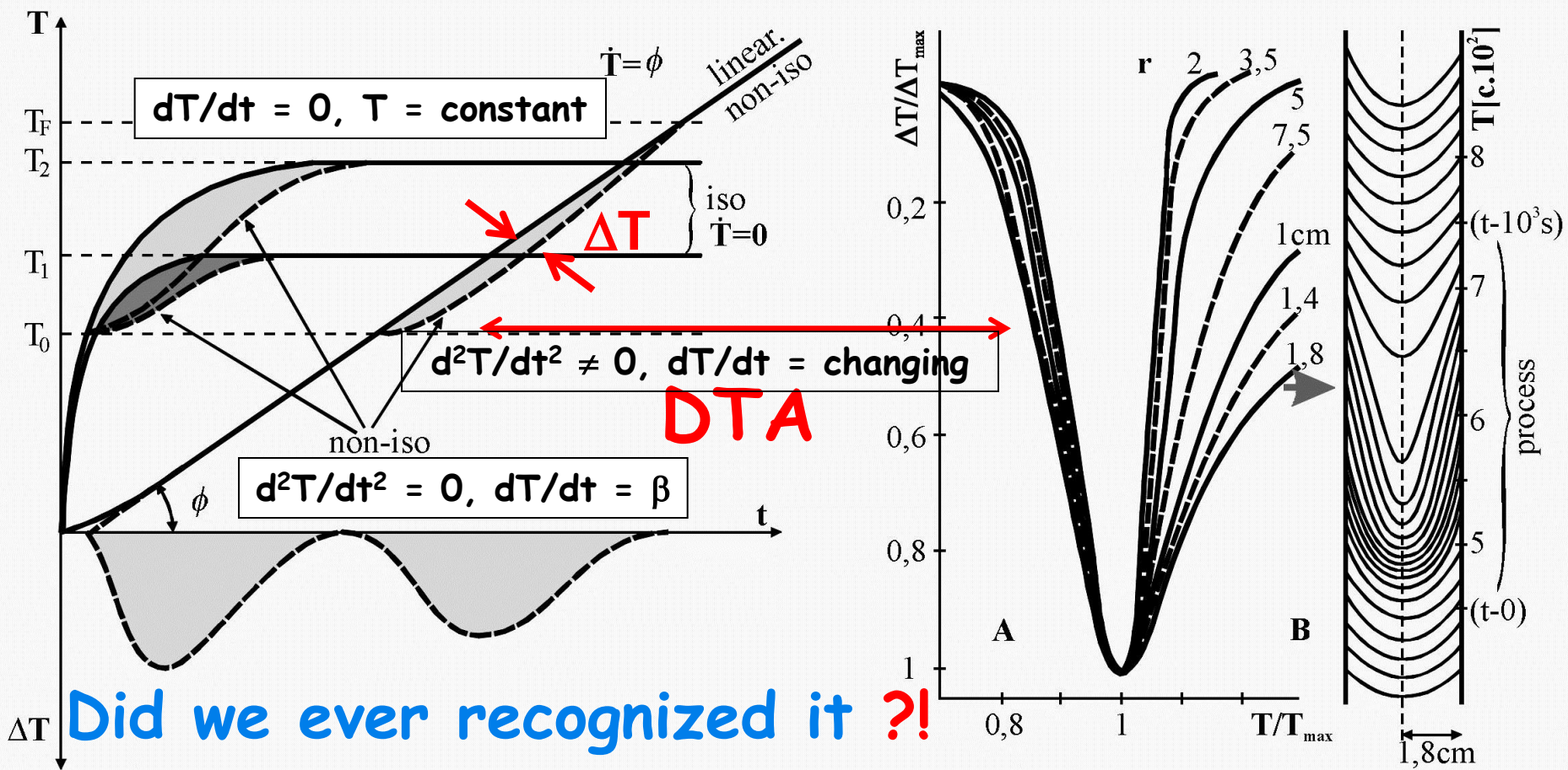
Why are the curves/peak by DTA and DSC different ?

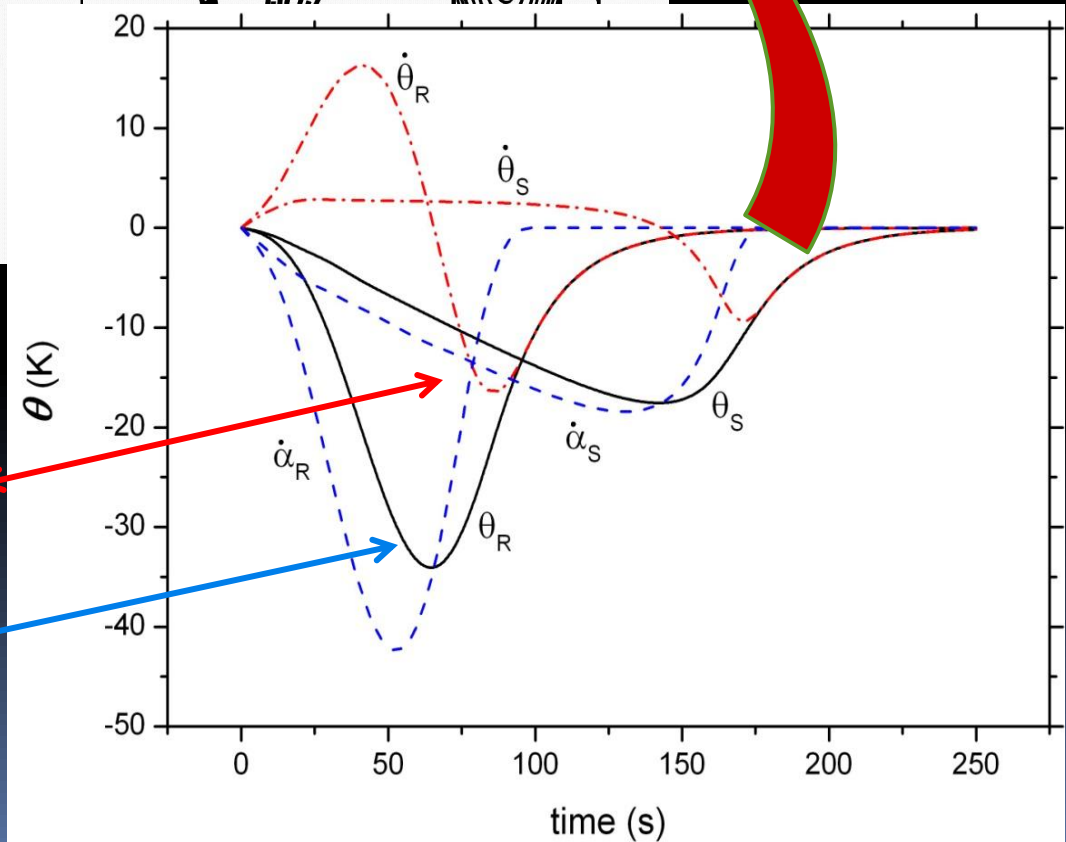
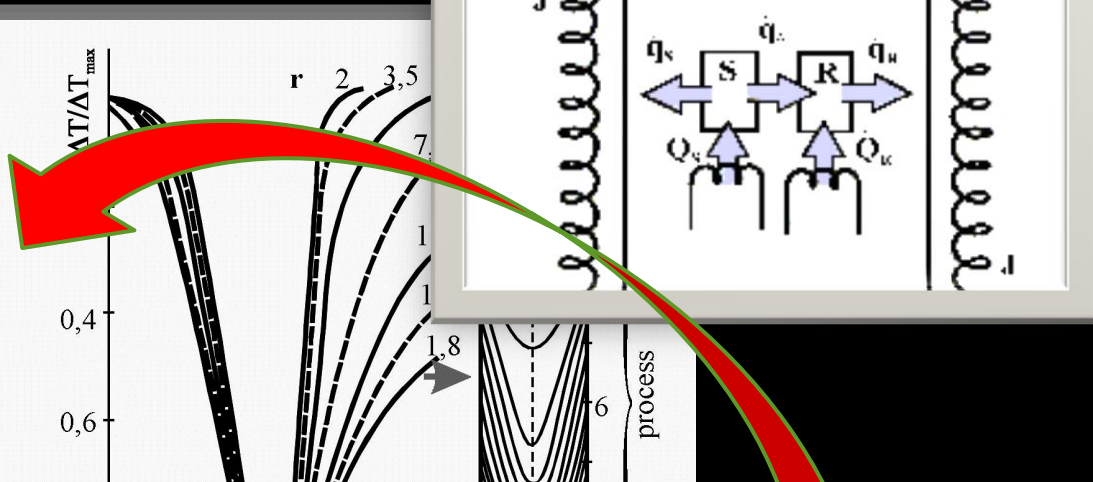
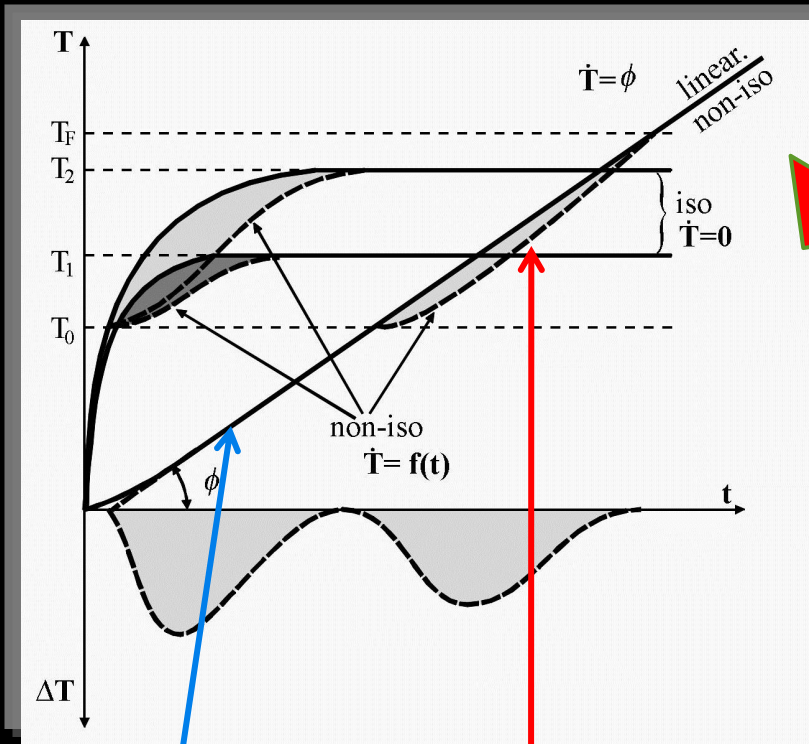
Mutual comparison of the sensitivity of measurements



Can we recognize its consequences ?!

Isothermal and non-isothermal measurements: naturally involves thermal setups-gradients

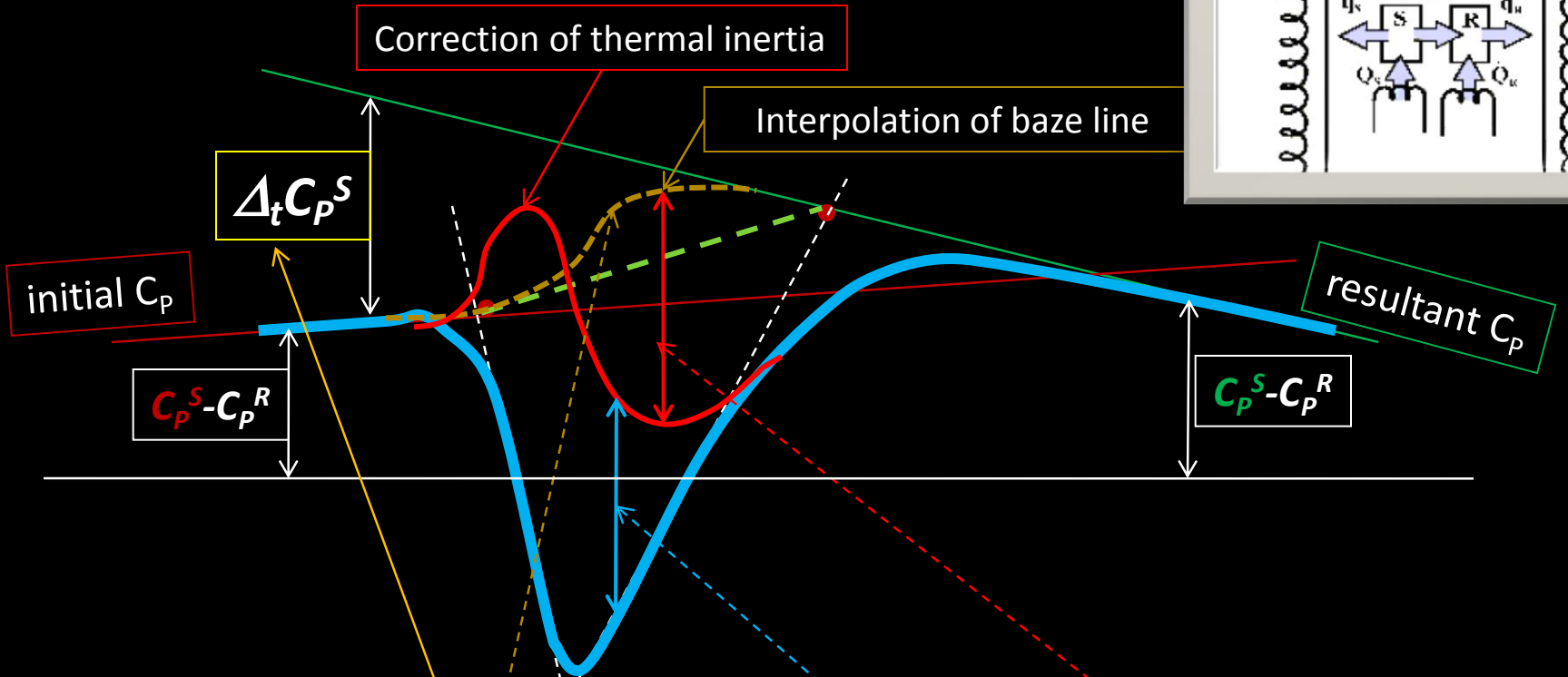
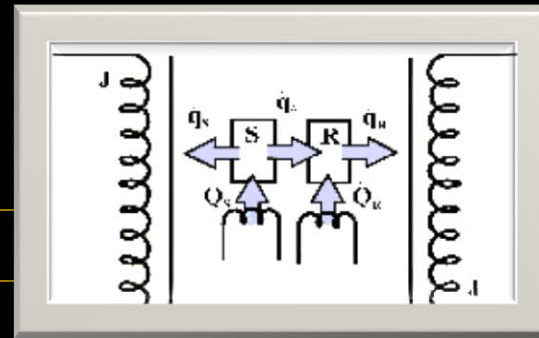




Relate to the peak background temperature

Relate to linearly increasing external temperature of heated furnace

DTA CURVE



$$\Delta T(t) \cdot K_S(T, \Phi) =$$

$$= \Delta K(T_O - T_R) - \Delta C_p \Phi + \Delta_t C_p^S (1 - \alpha) (\Phi + d\Delta T/dt) - \Delta_t H^S (d\alpha/dt) - C_p^S (d\Delta T/dt)$$

DTA equation

Thermal capacity of sample

Effect of heat inertia on kinetic evaluations



Evaluation of kinetics and mechanism by SQUEST
Škvára F, Šesták J. Computer calculation of the mechanism and associated kinetic data using a non-isothermal integral method J. Thermal Anal. Calor. 1975; 8: 477-489

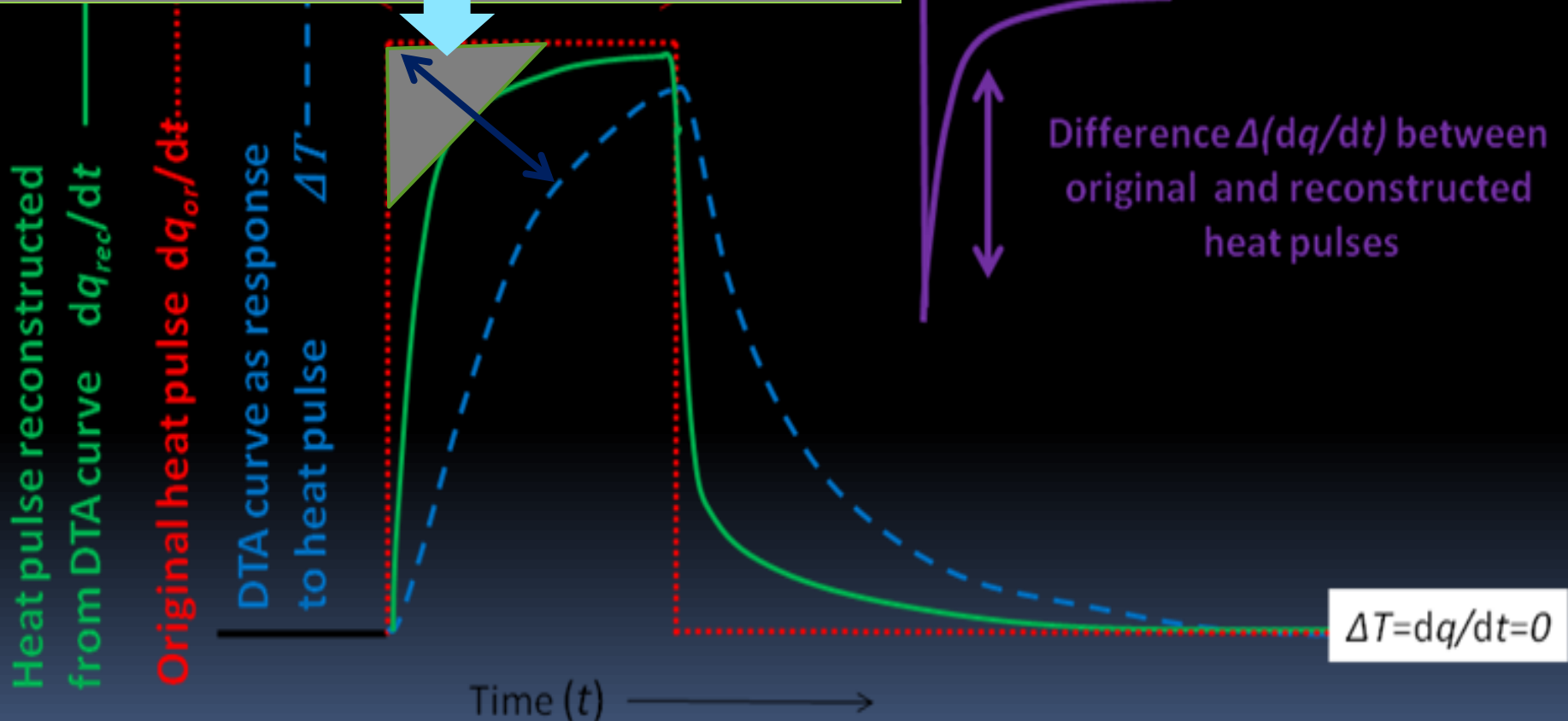
Phase transition of BaCO₃ at 810° C

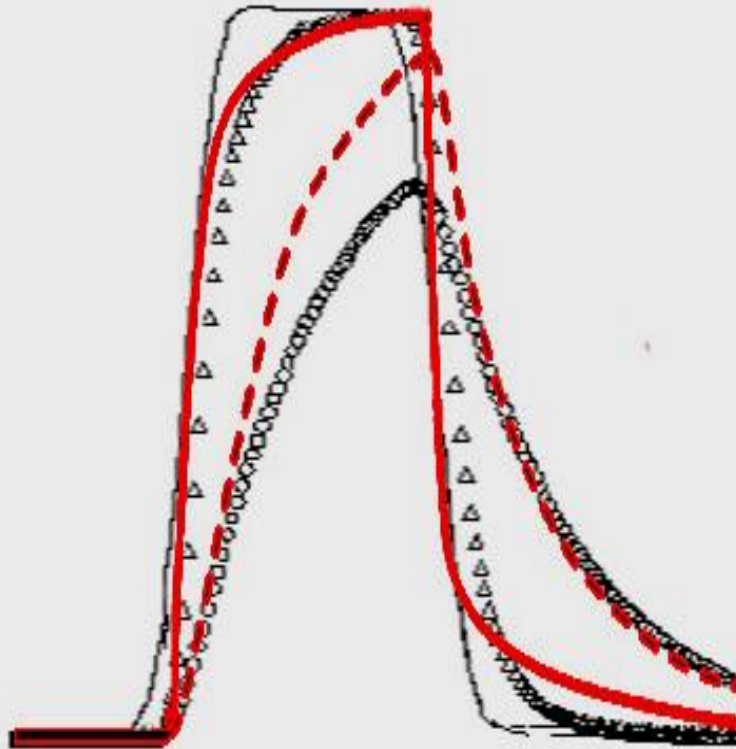
ΔH	E [cal]	mechanism
613	118	A3
617	52	A3

Inertia rectifying evaluation program by ALANTA :
Holba P, Nevřiva M, Šesták J. Analysis of DTA curve and related calculation of kinetic data using computer technique. Thermochim. Acta 1978; 23: 223-231.

Gradient rectification by introducing an additional correction term respecting the changes in temperature field inside the sample $d\theta_{SM}/dt$, where θ_{SM} is the difference between the surface-measured temperature and the temperature averaged over the whole volume of sample

Practical approval and T-gradients





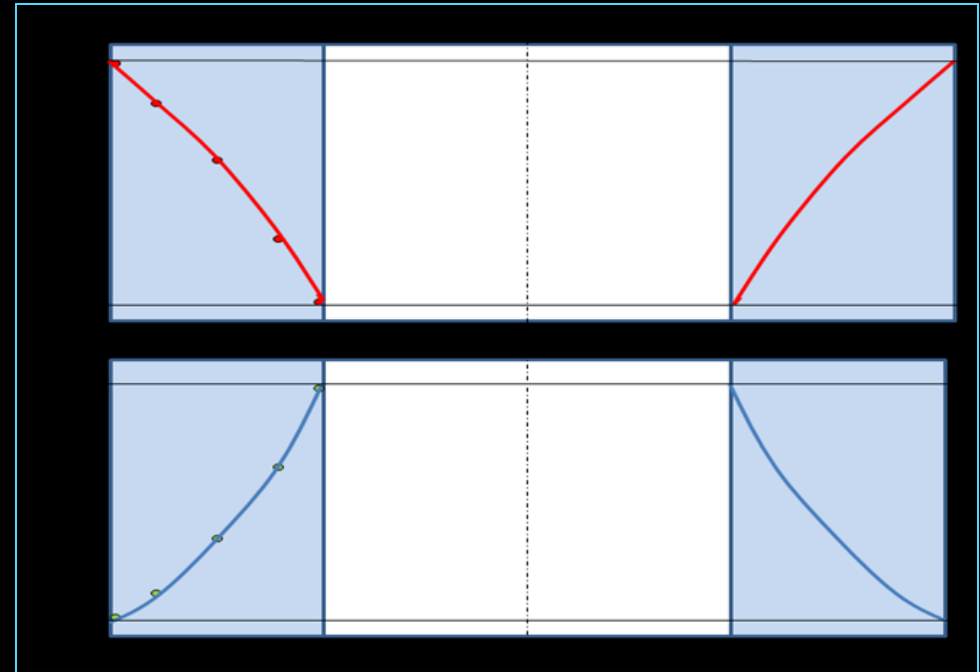
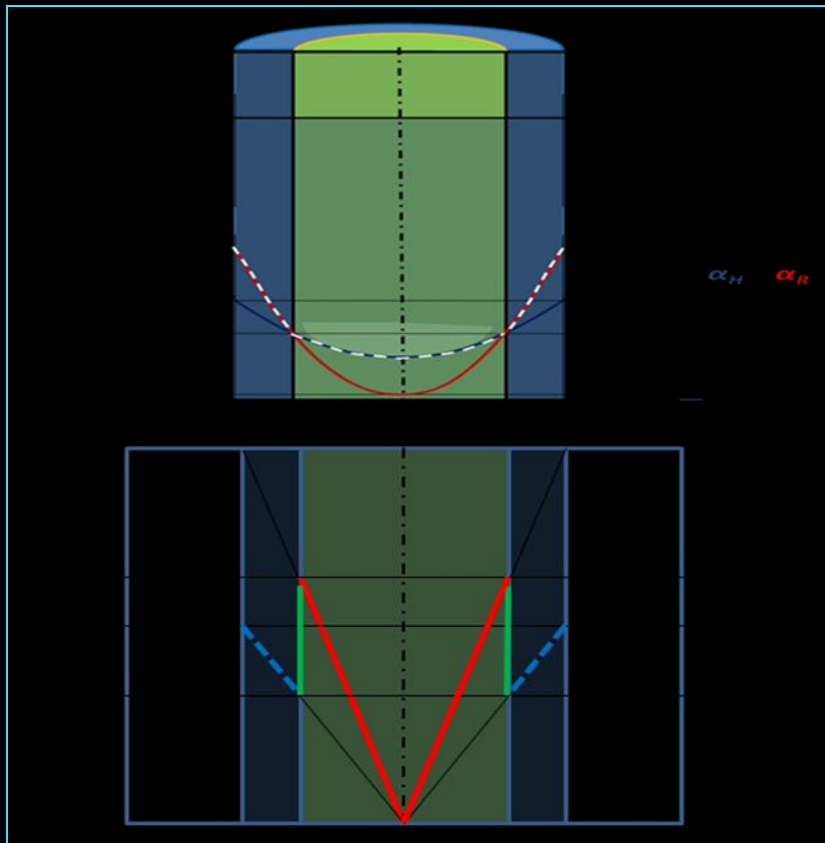
Holba P, Šesták J, Sedmidubský D (2013) **Heat transfer and phase transition at DTA experiments.**

Chapter 5 in: Thermal analysis of micro-, nano- and non-crystalline materials (J. Šesták, P. Šimon.

Eds), Springer, Berlin, pp. 99-134

A rectangular heat pulse was inserted into the sample by either method: (a) circles - the resistant heating inside the sample under the mode of linear heating and (b) triangles - the heat irradiation on sample surface during the isothermal regime. Both pulses are normalized on the $\langle \Delta T \text{ vs. } t \rangle$ axis as to fine-tuning the same shape. The as-measured DTA response on the internally inserted pulses (dashed red line, resistant heating) was corrected on the heat inertia effect by differential method to yield the rectified peak (full red line). The as-measured DTA feedback on the externally applied heat-pulse (small-circle line) was corrected by the standard Netzsch instrumental software based on integral method giving a rectified peak (small-triangles line). Both rectifications emerge the matching character of corrections. The upper left area between rectified peak and inserted rectangular pulses results from yet uncorrected temperature gradients in the sample

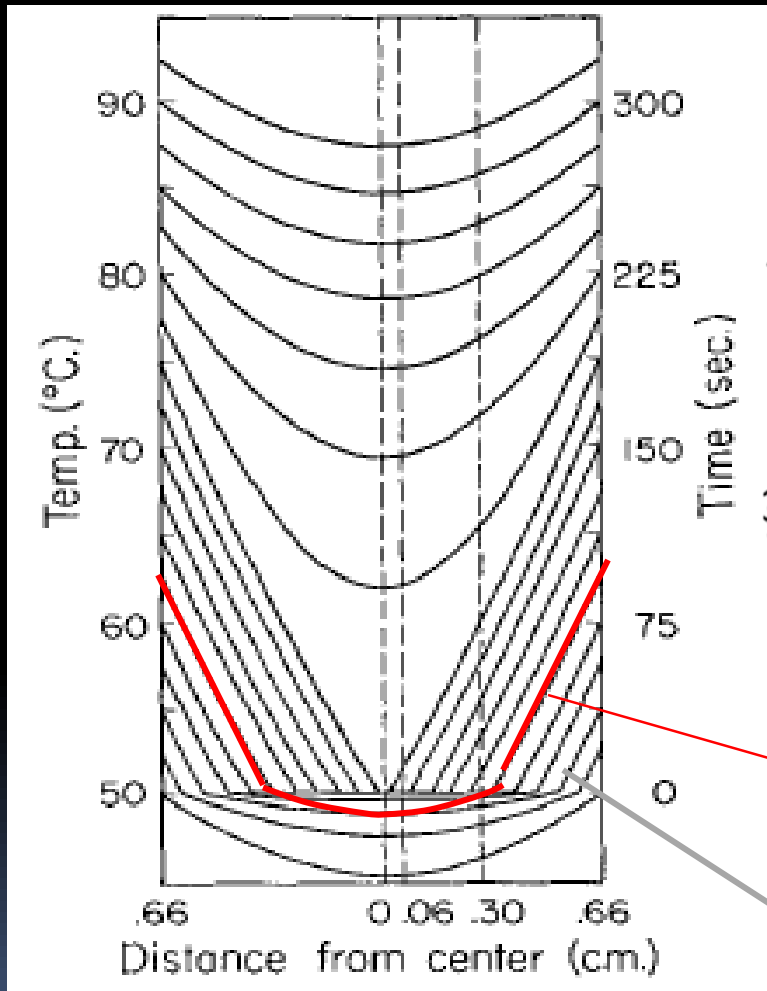
Temperature profiles



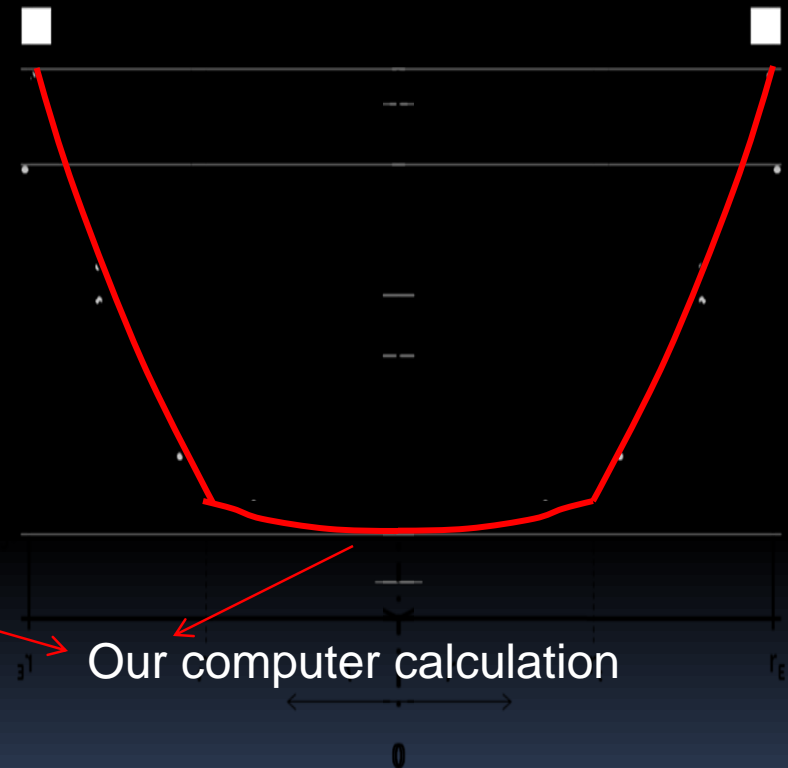
Stabilized temperature profiles $T_R(r)$, $T_H(r)$ and gradient profiles $g_R(r)$, $g_H(r)$ at linear heating ($\Phi_{RE} > 0$) in an infinite cylinder with external radius of holder (jacket) r_H and external radius of reference (core) r_E in the case when the thermal diffusivity of holder material α_H is greater than that of the reference material α_R ($\alpha_H > \alpha_R$).

Stationary temperature profile $T_R(r)$ and gradient profile $g_R(r)$ in hollow cylinder with outer radius r_E and inner radius r_I separating outer reservoir with temperature T_E and inner reservoir with temperature T_I

Temperature profile according to Smyth compared with our continual model utilized by computer calculus



1951 data



Our computer calculation

Smyth HT. *Temperature Distribution during Mineral Inversion and Its Significance in DTA*. J. Amer. Cer. Soc. 1951; 34: 221-224.

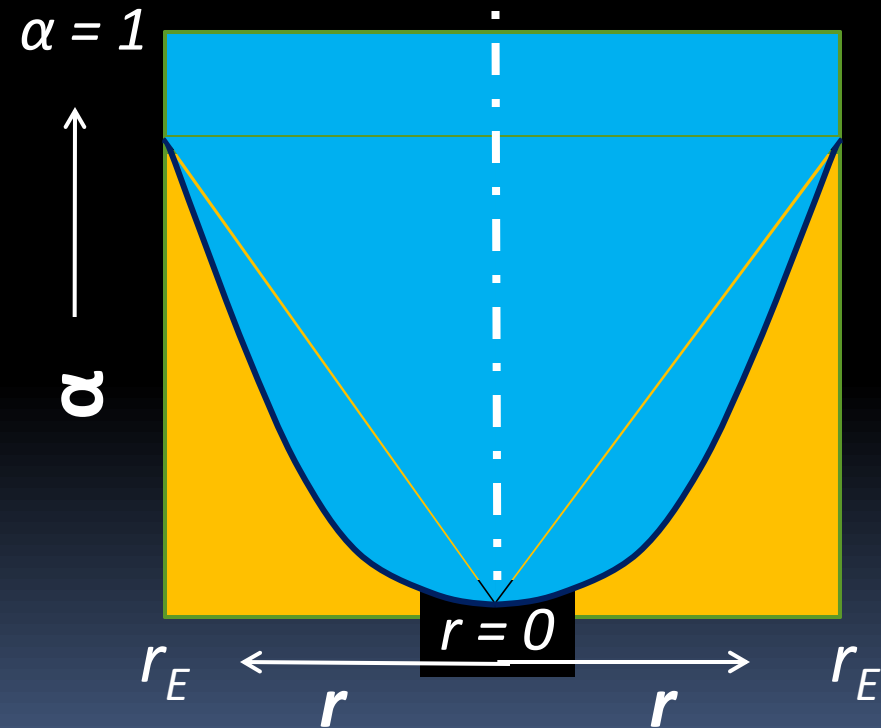
Kinetic models of a phase transition

(initial)

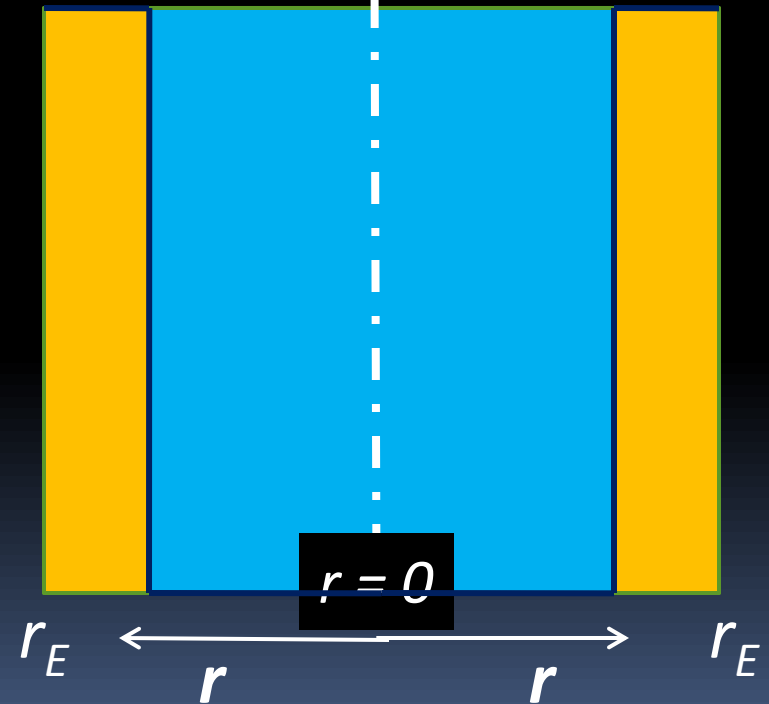
(final)

Continual model:

Discontinual model:



α



Courtesy by Pavel Holba

Variants of kinetic models of a phase transition

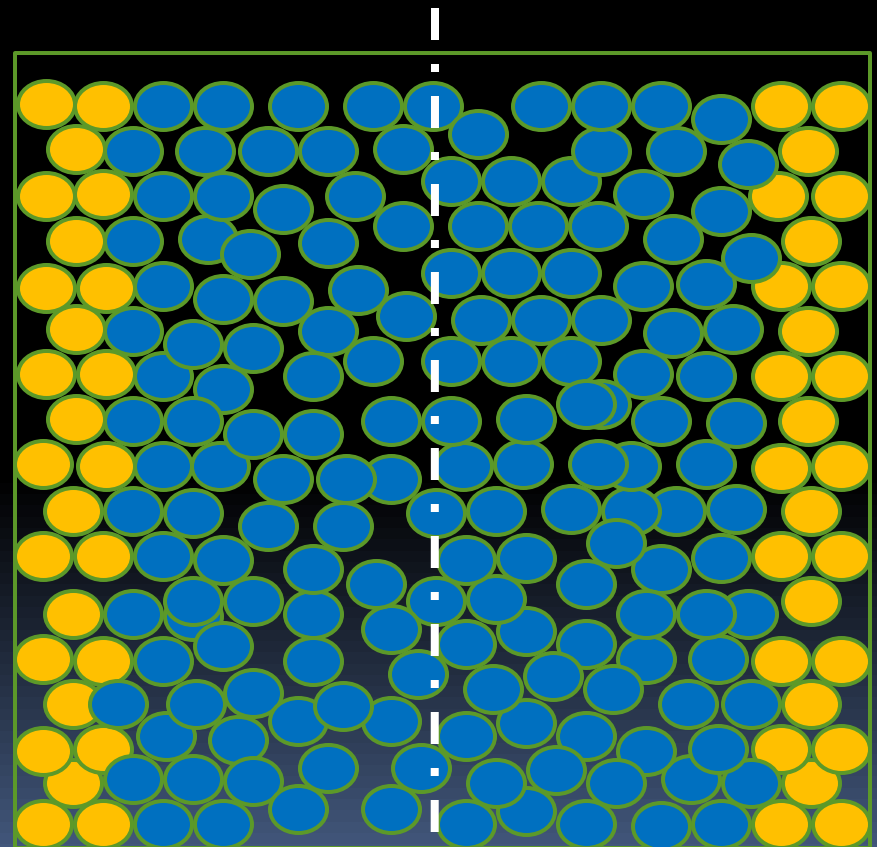
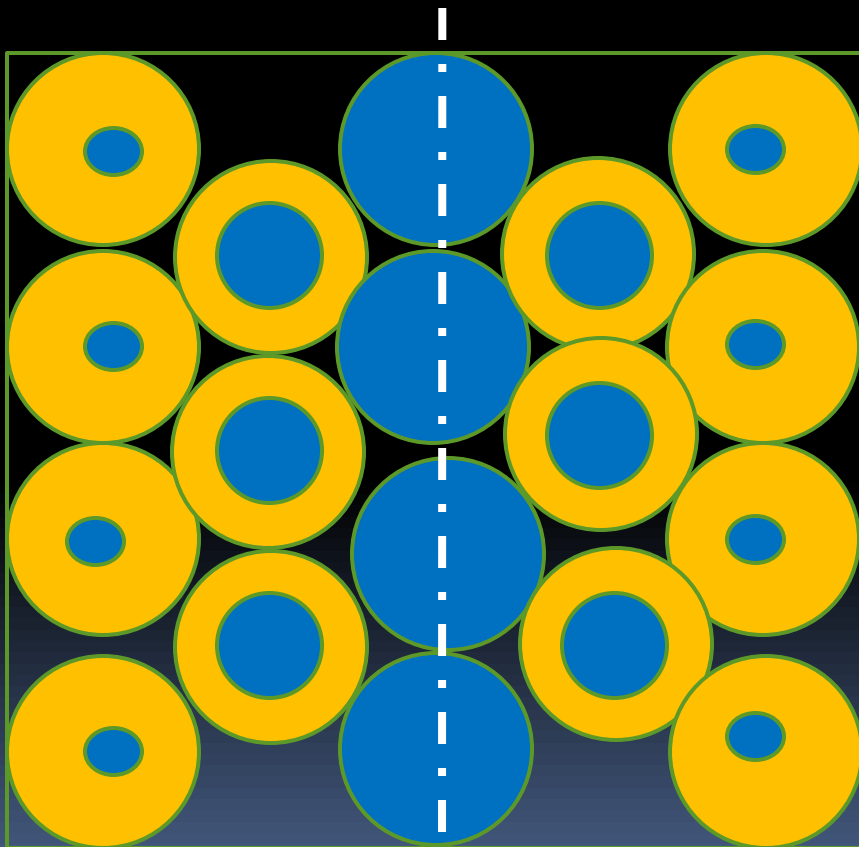
(initial)

&

(final)

continual model:

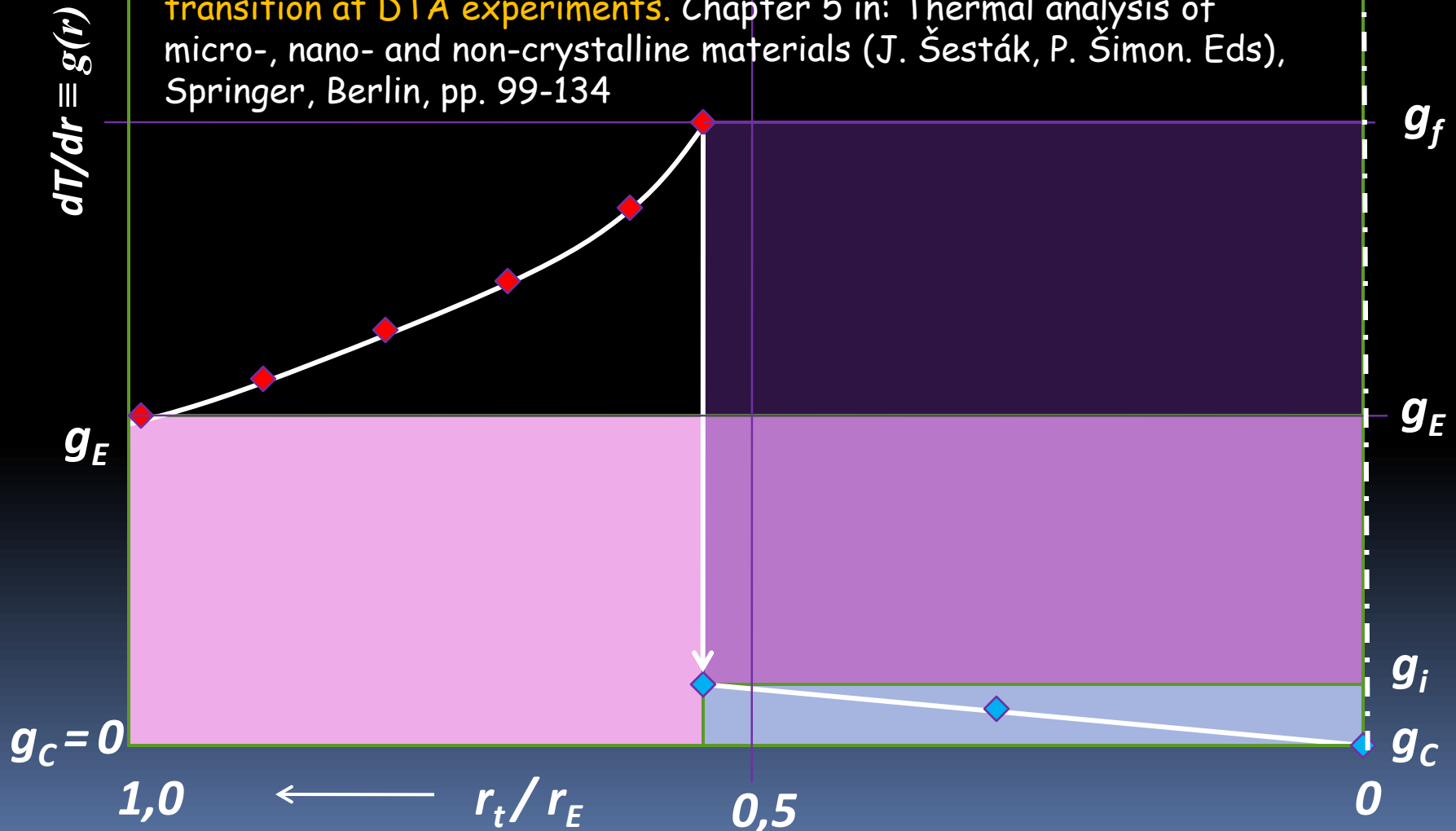
Discontinual model:



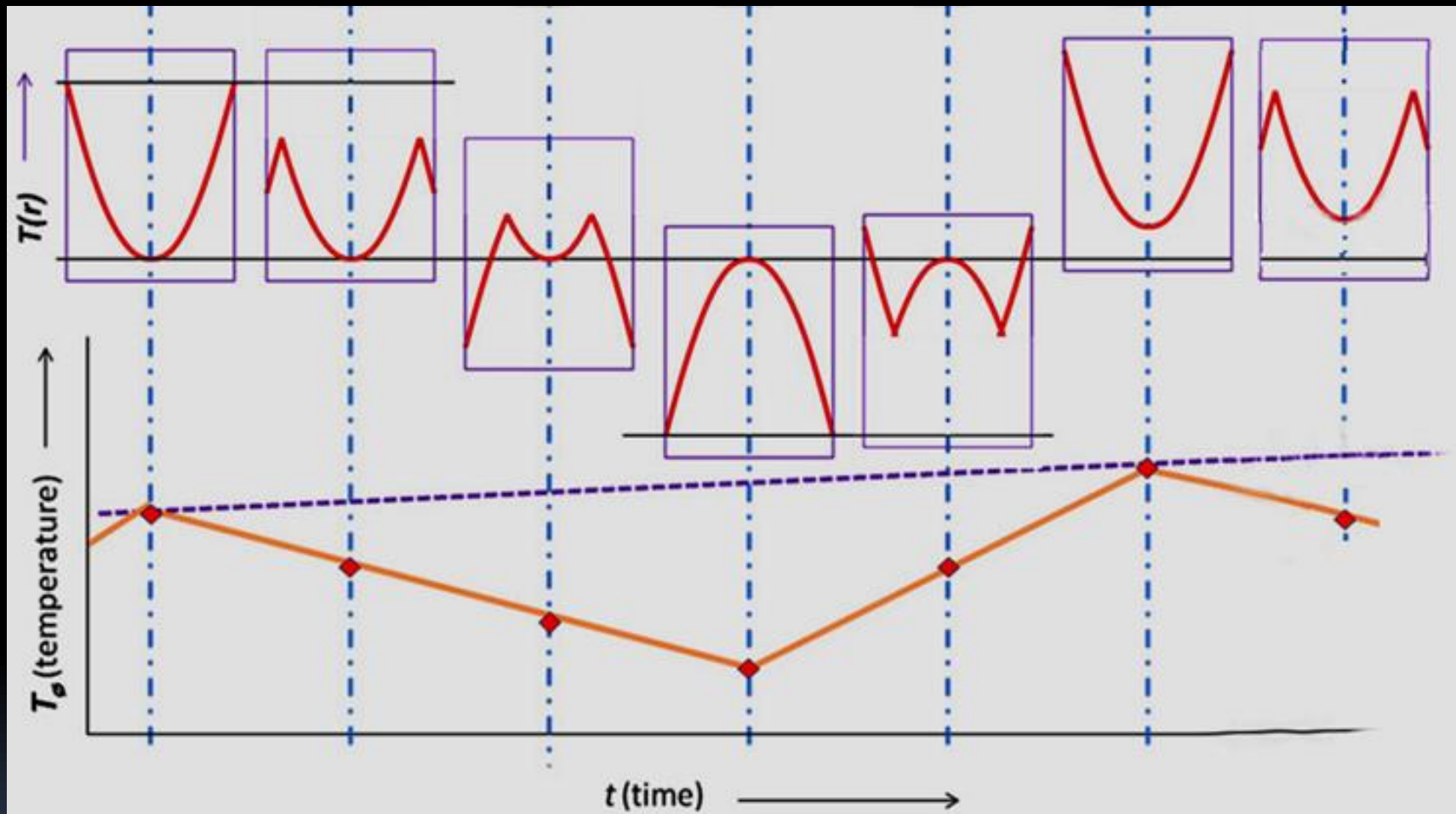
Courtesy by Pavel Holba

Profile of temperature gradient in the sample at the degree of transition $\xi = 0.7$ assuming a discontinued model

Holba P, Šesták J, Sedmidubský D (2013) *Heat transfer and phase transition at DTA experiments*. Chapter 5 in: Thermal analysis of micro-, nano- and non-crystalline materials (J. Šesták, P. Šimon. Eds), Springer, Berlin, pp. 99-134



Thermal gradients appear everywhere even during small temperature alternations in modulated thermal analysis



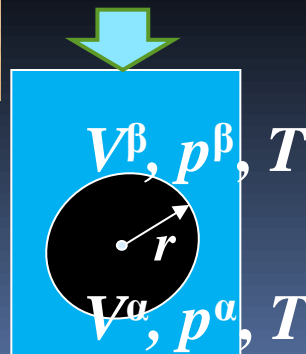
Holba P, Šesták J, Sedmidubský D (2013) **Heat transfer and phase transition at DTA experiments**. Chapter 5 in: Thermal analysis of micro-, nano- and non-crystalline materials (J. Šesták, P. Šimon. Eds), Springer, Berlin, pp. 99-134

What is temperature under extremes?

Size and speed matters

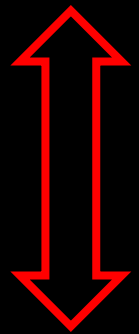


Current study exploring dimensionality changes, impact of surface tension



Macro extreme astrophysics

Extreme temperature changes

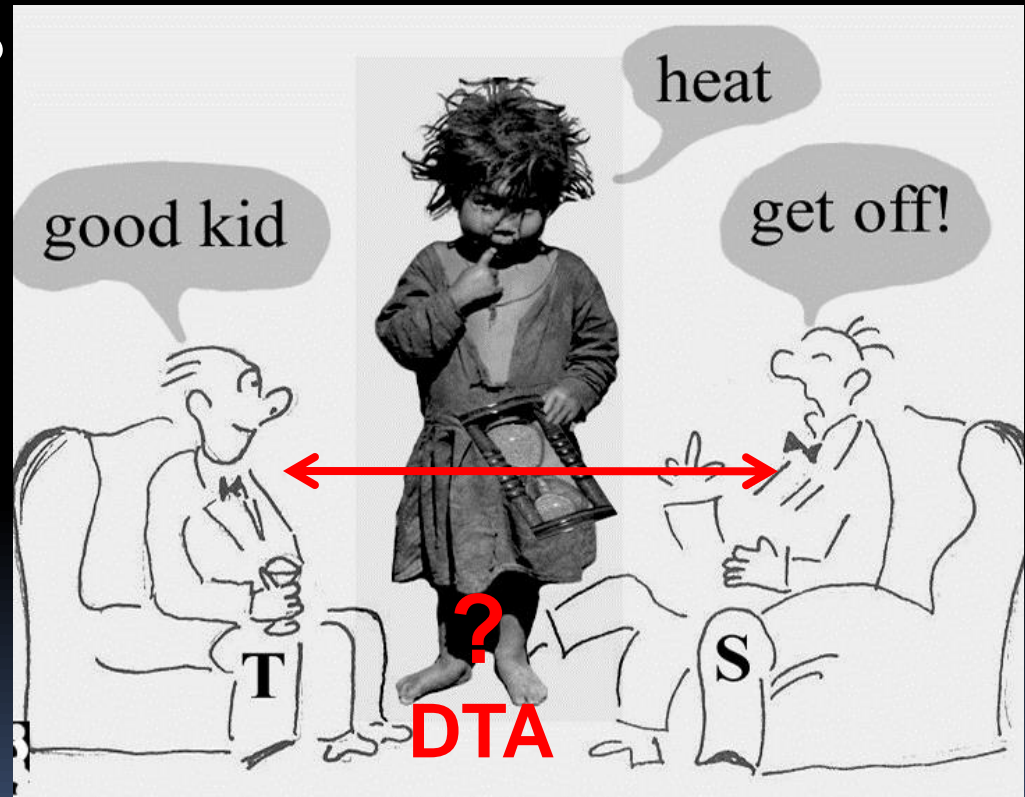
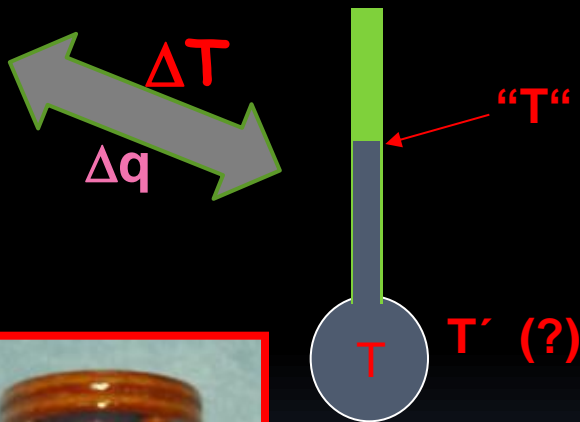


Micro extreme nanophysics

Ultra-fast processes - what is temperature contrivance of thermodynamics

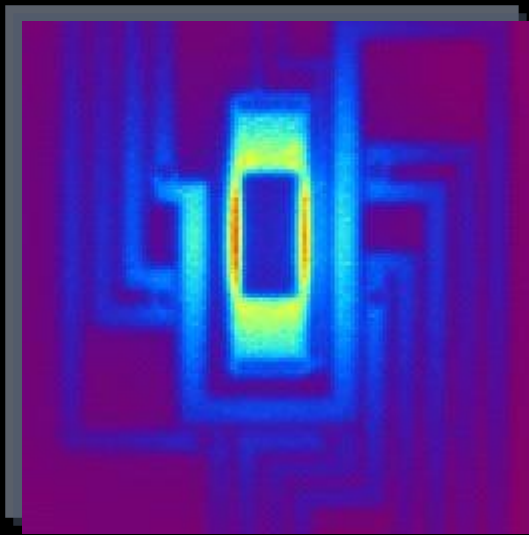
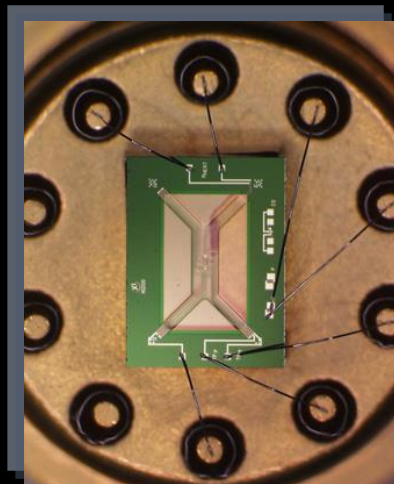
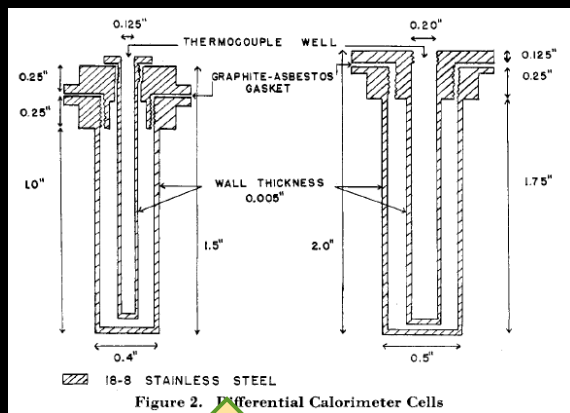
What happens if there
is no time for the system
fast-enough equilibration?

↓ **Thermostatics** Heat transfer **Thermotics** ↓

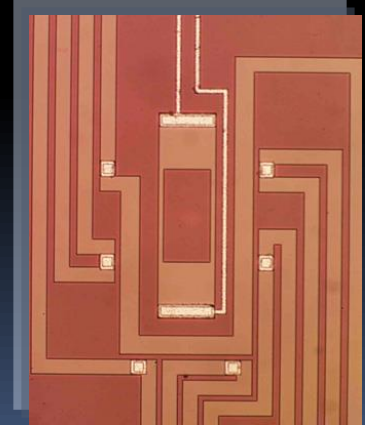
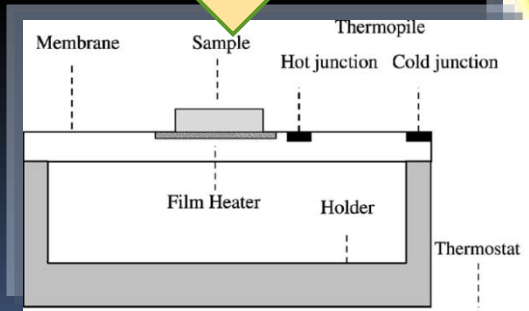
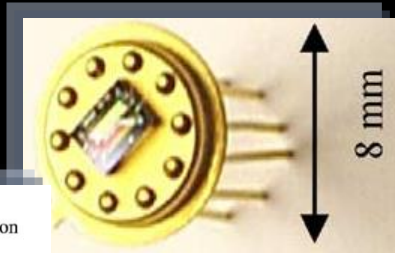


what says "each thermodynamics" ?

Not knowing well the thermal nature in a classically arranged sample we are seeking for yet novel methods applying more and more complex regimes



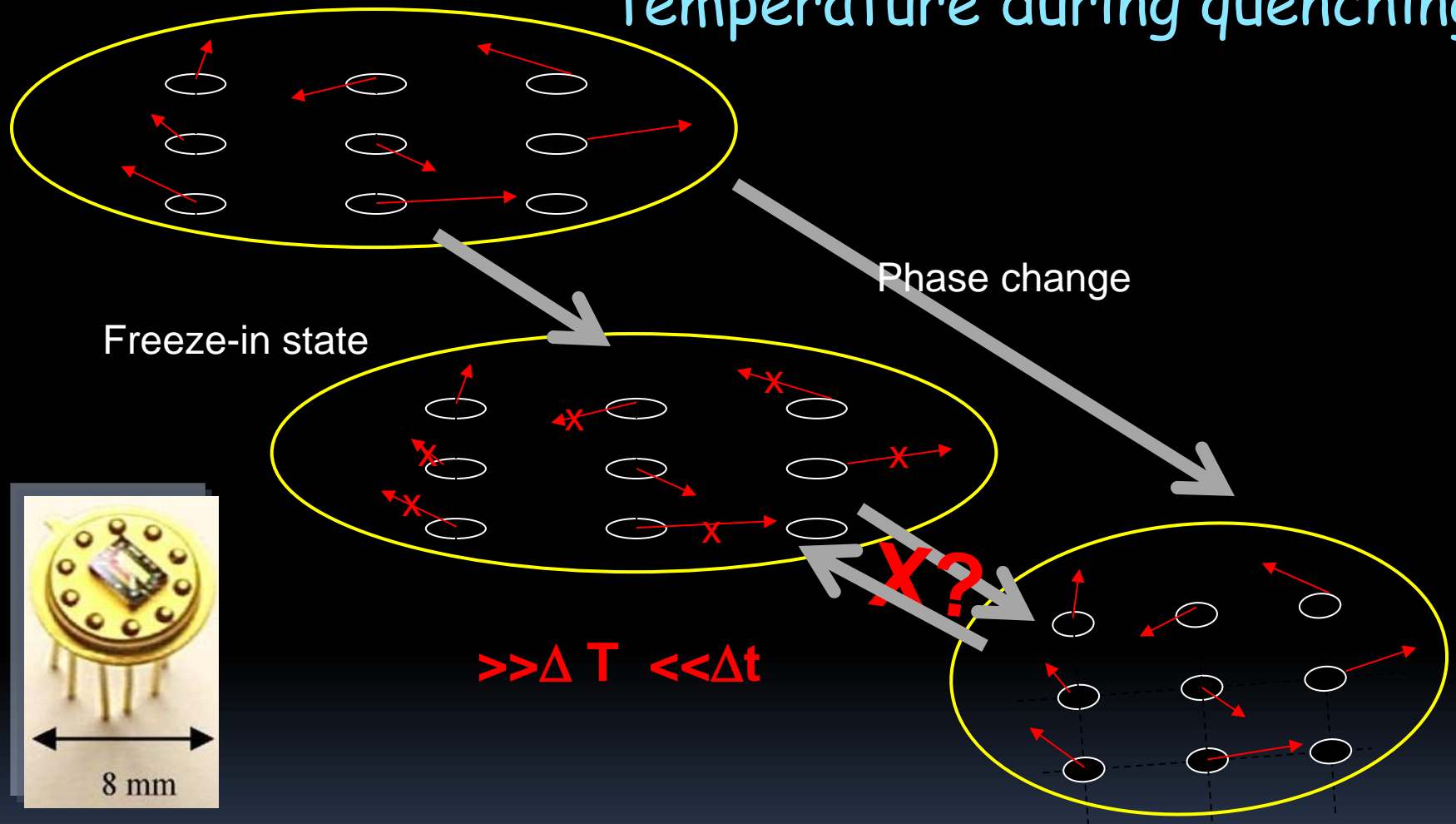
MICROCHIPS



Amplitude of the radiation intensity $I(x, y)$ measured at ac heating (2 V, 1 Hz). Dashed line A indicates the direction at $y_1 = -24 \mu\text{m}$ along which the dependence $I(x, y_1)$ was measured.

S.A. Adamovsky, A.A. Minakov, C. Schick. *Scanning microcalorimetry at high cooling rate*. *Thermochimica Acta* 403 (2003) 55–63; and: *Ultra-fast isothermal calorimetry using thin film sensors* *Thermochimica Acta* 415 (2004) 1–7

Special case of a change: temperature during quenching



Šesták J (2016) Measuring "hotness", should the sensor's readings for rapid temperature changes be named "tempericity"? J Therm Anal Calorim 125: 991–999

Holba P (2016) Šesták's proposal of term „tempericity“ for non-equilibrium temperature and modified Tykodi's thermal science classification with regards to methods of thermal analysis. J Therm Anal Calorim. 2016

Temperature -tempericity of ultrafast changes (in nano-scale) and its determinability

$$\Delta q \Delta T = ?\Delta?$$

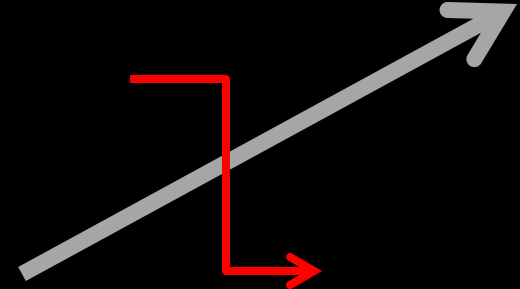
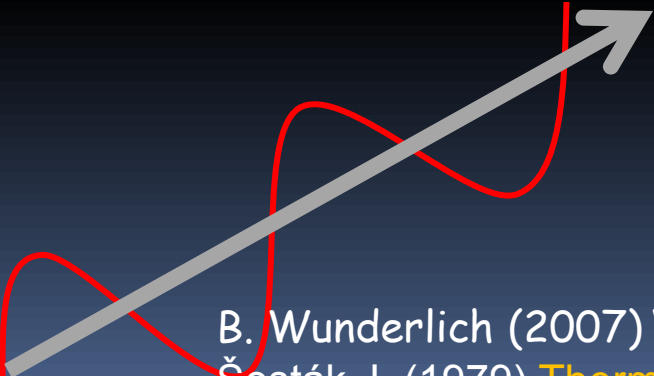
Where is the operate limit of
uncertainty principle

$$\Delta T/\Delta t = ?\Delta?$$

Where is the operate limit of ever
recordable temperature changes

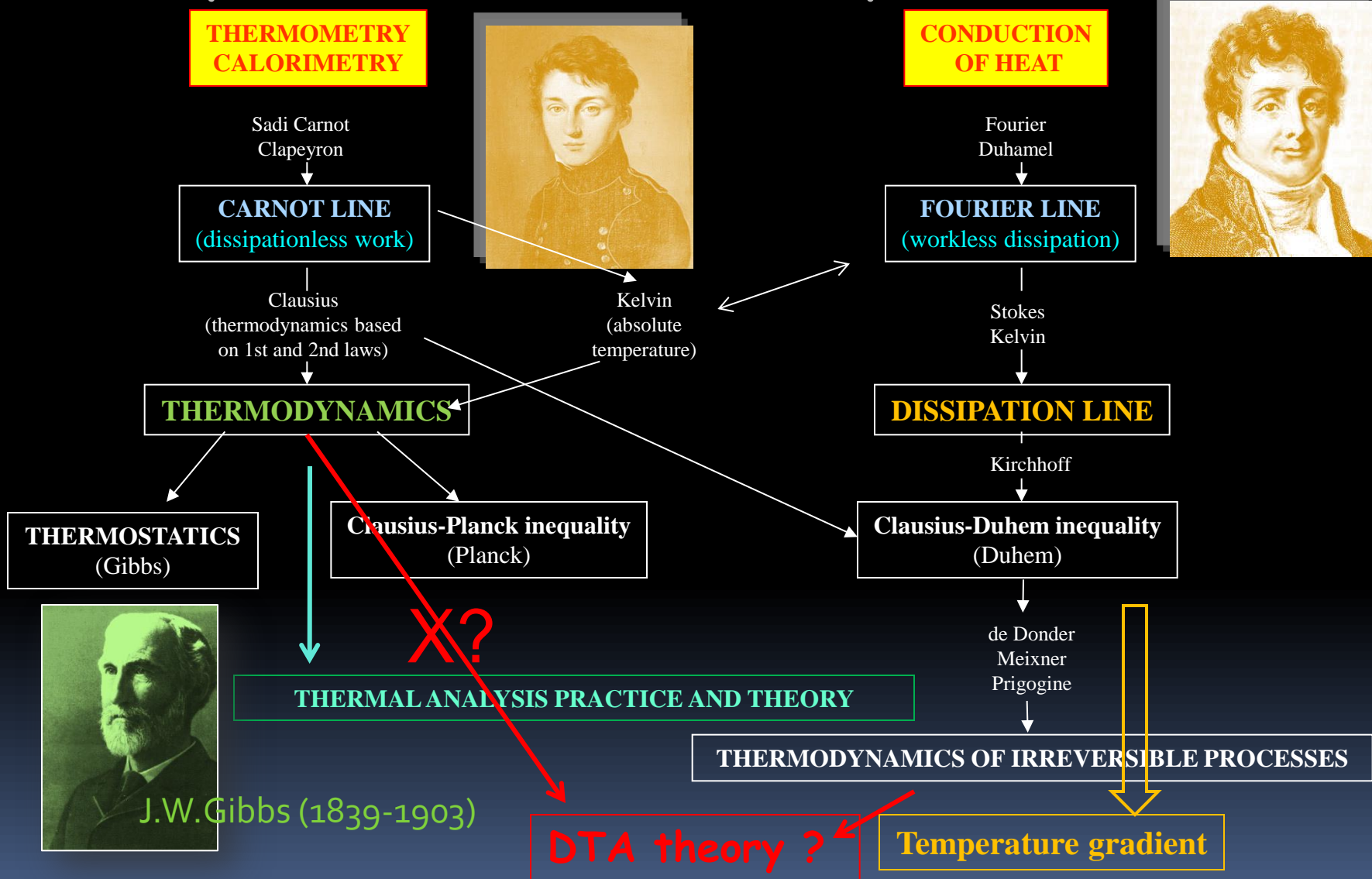
$$\Delta T = ?\Delta?$$

Where is the limit of readable and
reproducible temperature gradient



B. Wunderlich (2007) "Calorimetry of Nanophases "Int.J. Thermophysics 28 958-96
Šesták J. (1979) Thermodynamic basis for the theoretical description and correct
interpretation of thermoanalytical experiments. Thermochim Acta; 28: 197-227

Thermodynamic approach through the detailed analysis of family tree of existant thermodynamic subdivisions:



Holba P, Šesták J., (1976) "Theory and practice of DTA/DSC" Silikáty (Prague) 20: 83 (1976; and Quantitative evaluation of thermal effects: theory and practice. Annali di Chimica 67: 73 (1977)

Thermodynamic approach needing an extension for true non-equilibriums studies

THERMOMETRY CALORIMETRY

Sadi Carnot
Clapeyron

CARNOT LINE
(dissipationless work)

Clausius
(thermodynamics based
on 1st and 2nd laws) ↓

THERMOSTATICS
(Gibbs)

$$dT/dt = 0, T = \text{constant}$$

Temperature

CONDUCTION OF HEAT

Fourier
Duhamel

FOURIER LINE
(workless dissipation)

Stokes
Kelvin

Clausius-Duhem inequality
THERMODYNAMICS
of irreversible processes

$$d^2T/dt^2 = 0, dT/dt = \beta$$

DTA theory ?

COMPLEX IMPACTS

William Whewell
(1794-1866)

TYKOLDI LINE
thermo-dynamics

Ralph Tykodi
(1925-2009)

THERMOTICS
TERMOKINETICS

$$d^2T/dt^2 \neq 0, dT/dt = \text{changing}$$

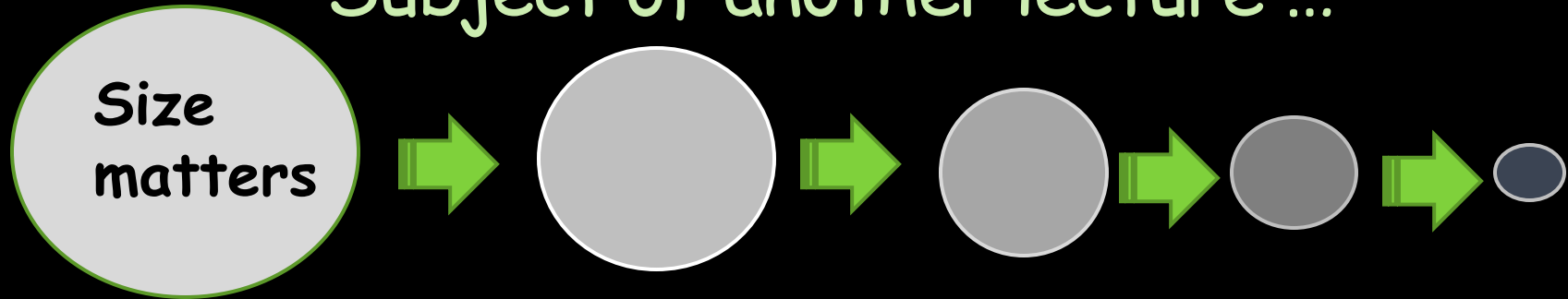
Tempericity

Temperature gradient

Yet uncertain territory of thermodynamics

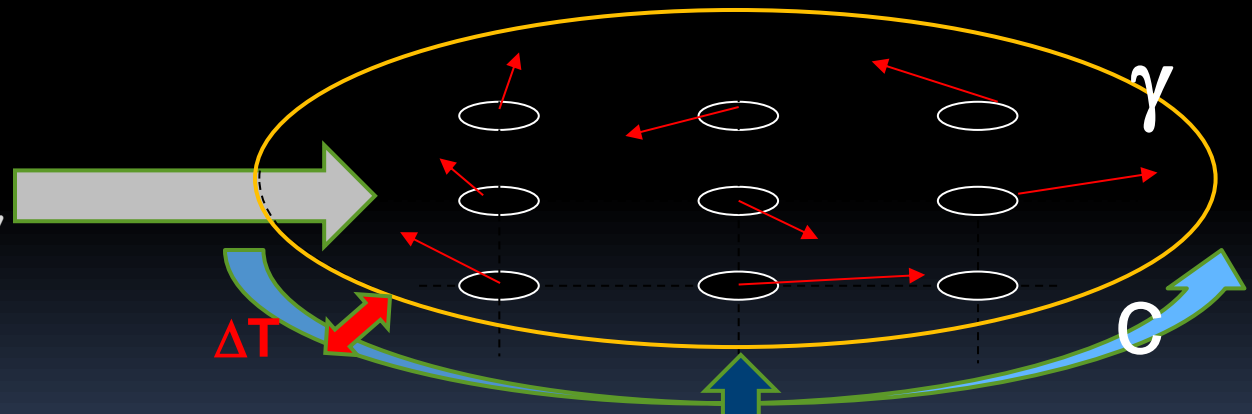
Corrections toward nano-scale progression ?

Subject of another lecture ...



At macroscopic scales: the Laws are perfectly valid for statistical systems but what happens at nano-scales (curved interfaces γ and c)?

Decreasing number of bulk molecules to a nano-limit narrowed by interface layer energy and curvature



$$T_{\text{non-eq}} = T_{\text{eq}} (2V \gamma / (\Delta H r))$$

Interaction between the sample holder (cell) and the entire sample surface
rivalry between the bulk $\sim r^3$ and surface $\sim r^2$

Quandary for diminutive bringing on micro/nano-analysis methods by using:

- * ultra-small samples and
- * mili-second time scales .

It involves a further peculiarity of truthful temperature (T_r versus T_∞) measurements of nano-scale crystalline samples in the particle micro range with radius (r) which becomes size affected due to increasing role of the surface energy usually described by an universal equation:

$$T_r/T_\infty \cong (1 - C/r)^p$$

where ∞ portrays a standard state and C and p are empirical constants ranging $\approx 0.15 < C < 0.45$ and $p = 1$ and/or $\frac{1}{2}$

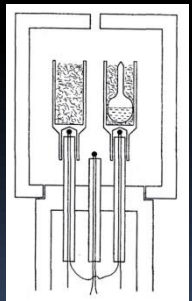
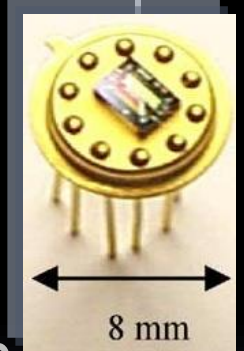
Šesták J. (2015) Kinetic phase diagrams as a consequence of radical changing temperature or particle size. J Thermal Anal Calor, 120: 129;

Any experiment **always** provides certain data on temperature and other measured variables \Rightarrow **sensor's reading!**

It seems that thermoanalysts believe that a mere **replacement** of thermocouples by thermocouple batteries or by highly sensitive electronic chips moreover renaming DTA principle to variously termed DSC's is a sufficient solution toward theoretical rations.

It's the **responsibility** of researcher to know to what extent spans his true conscientiousness!

One never gets to see that his work is so **secret** that he does not even know what he is doing!
(~allied to blindness trust to instrumental outputs)





inspirational links to Pavel Holba (1940-2016) legacy again

Pavel měl svoji logiku, v našem kabaretu 'Major Kopřiva' říká:
...aby se nemohl oheň rozšířit na odlehlejší místa, musí se nádoby se stlačeným plynem a veškeré hořlavé kapaliny neprodleně umístit do centra požáru!!...

a svá pozorování třídil podle principu:

....že každá myšlenka má poločas rozpadu, kdy se stává blbostí a naopak, každá blbost se po čase stává myšlenkou!!...

Chybíš nám Pavle !!

Díky za slyšení!

