

Temperature - its meaning claim under unsteady (and even extreme) conditions: from Newton cooling law to theoretical thermal analysis and further on ...

Jaroslav Šesták, Pavel Holba

New Technology - Research Center in the Westbohemian Region, West Bohemian University, Universitni 8, CZ-30114 Plzeň;



and Joint Laboratory with the Institute of Physics of the Academy of Sciences ČR, Cukrovarnická 10, CZ-16200 Praha, both Czech Republic; E-mail: sestak@fzu.cz

Санкт Петербург, Сентябрь 2013
St Petersburg , September 2013

with
← Igor Archangelski
and Jurij Metlin ↓



Dedicated to Pavel Holba



Holba last conference
CEEC Ljubljana 2015

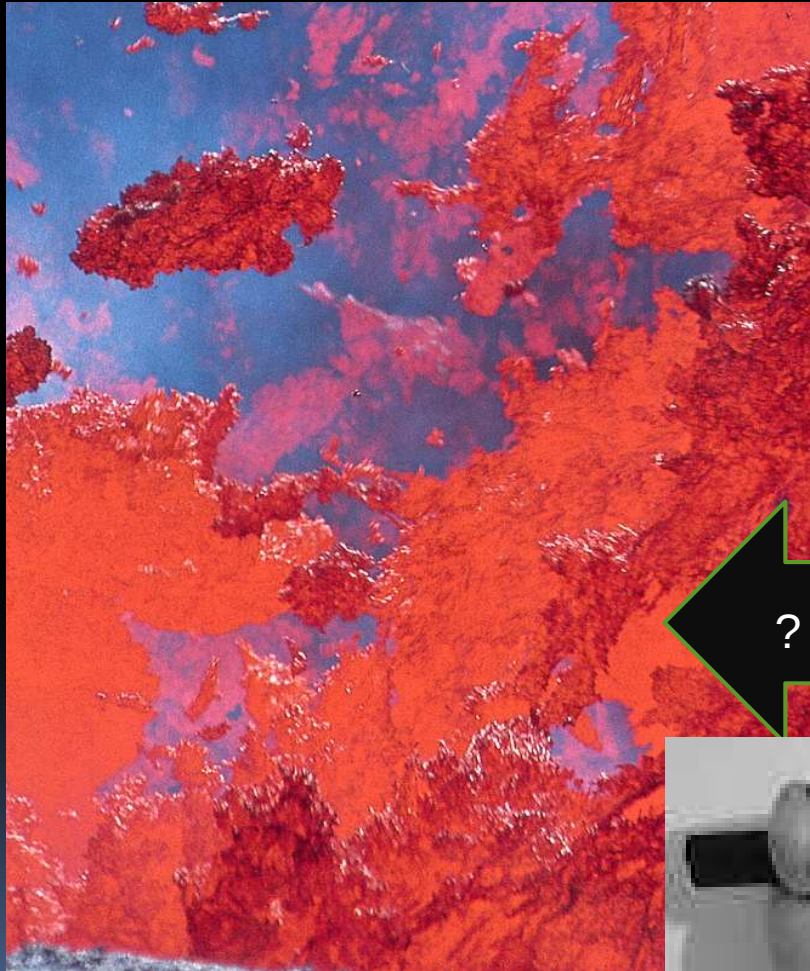


NTC - With Broněk Foller

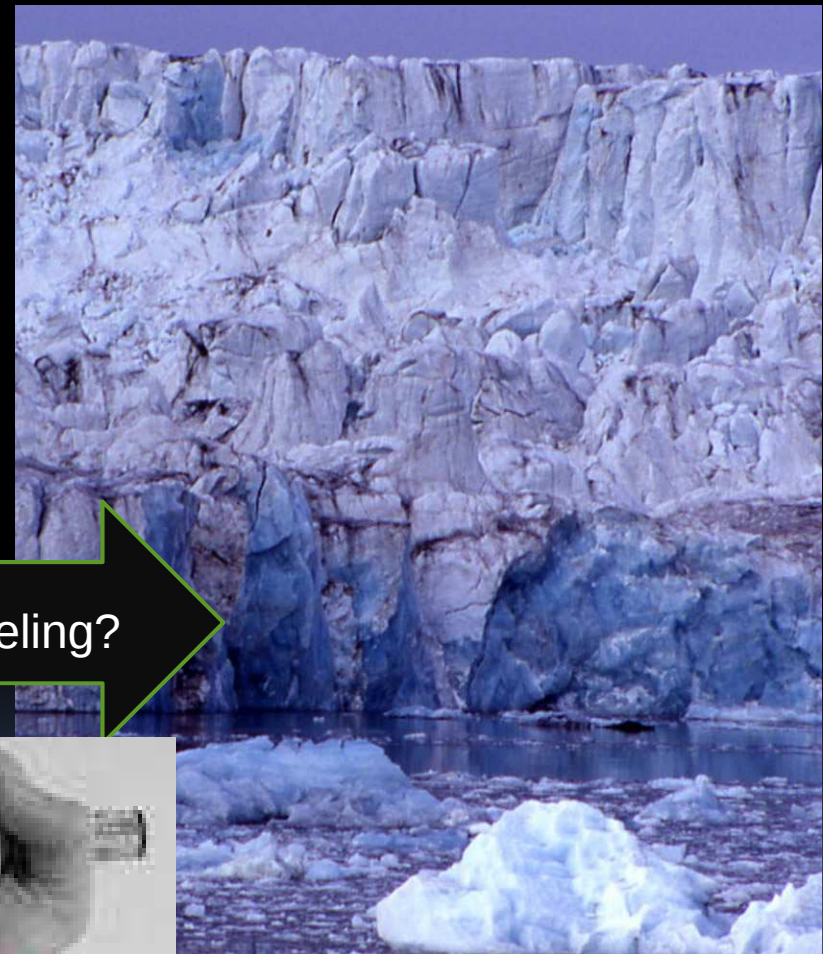
Co je teplota – naše cítění ?

heat = fire

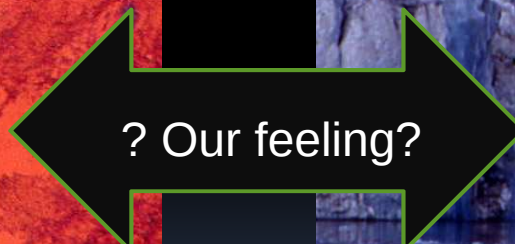
cold = ice



Wood-worm

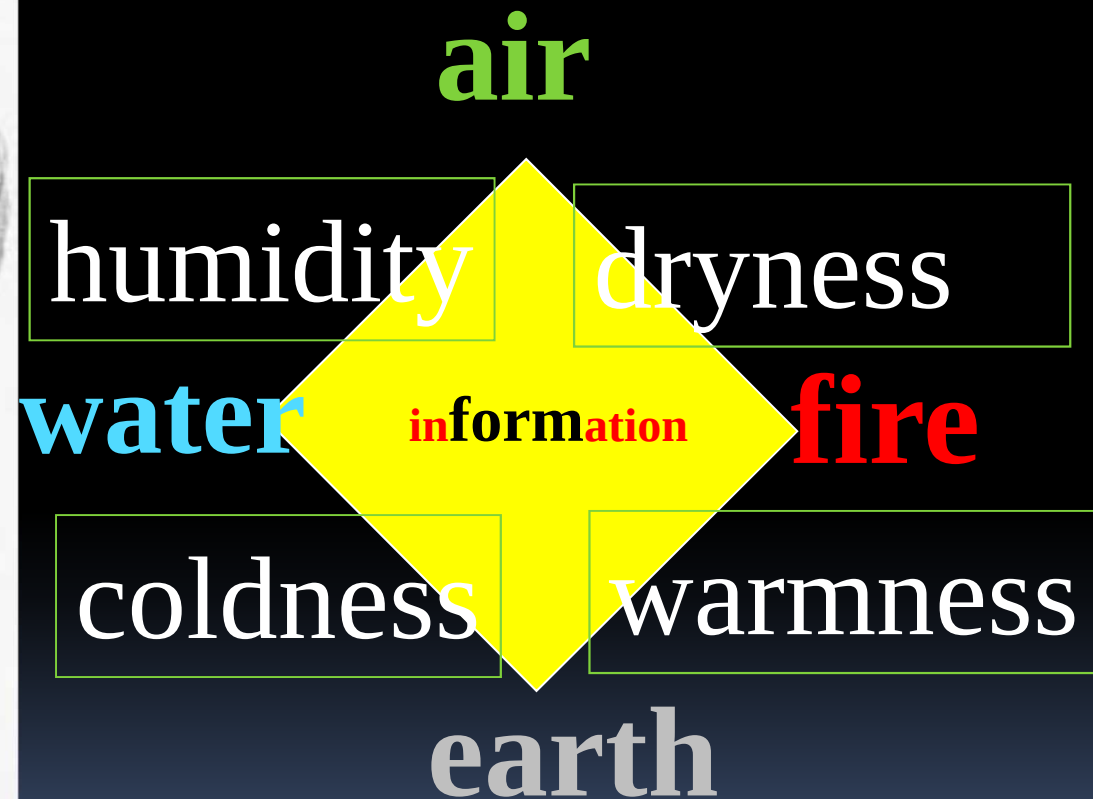
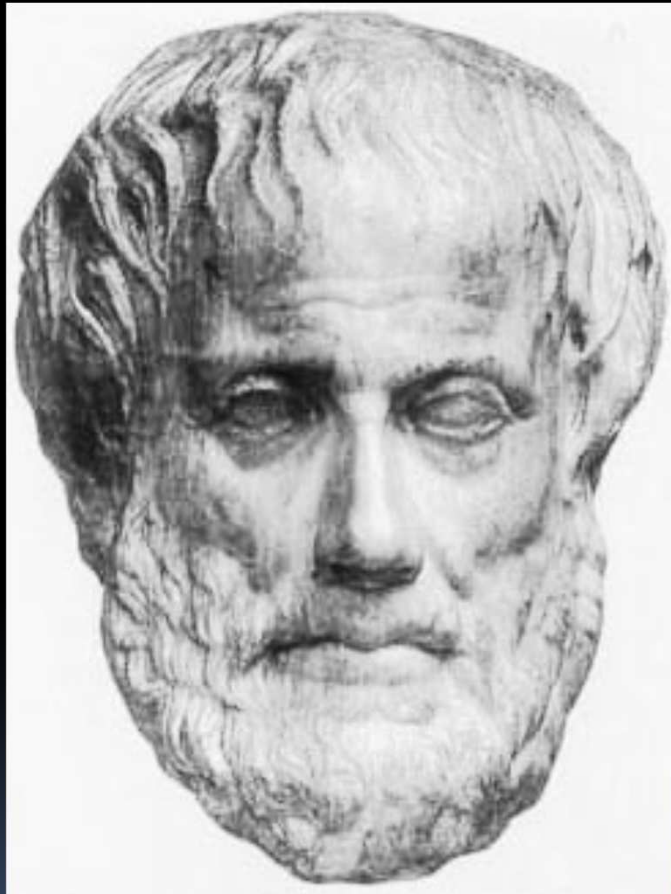


Metal- cold



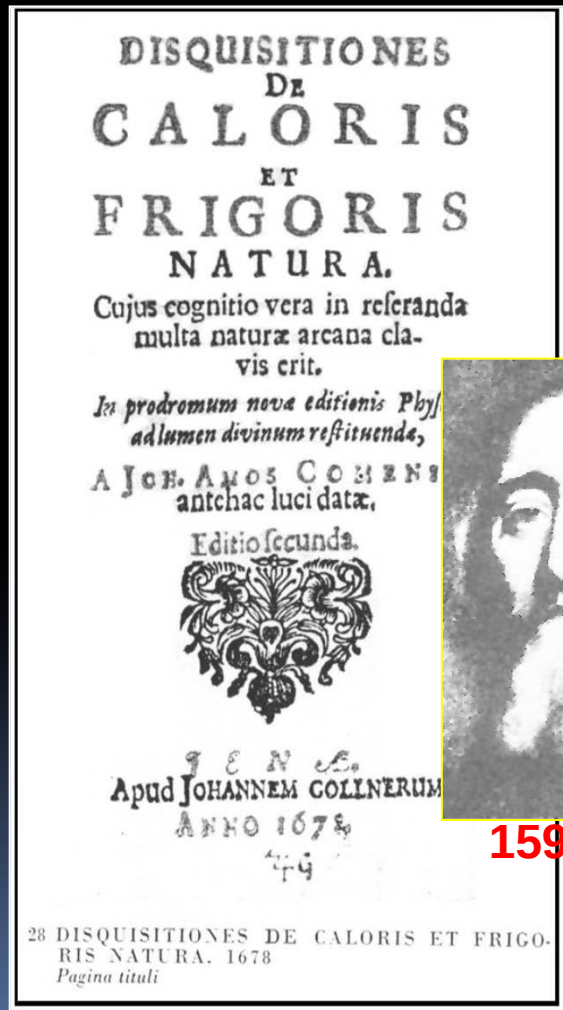
Holding a bar of ...

Qualities and quantities in Greek philosophy



Aristoteles 384 - 322 BC ($\Rightarrow$ thermal physics ?)
not distinguishig heat and temperature yet

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

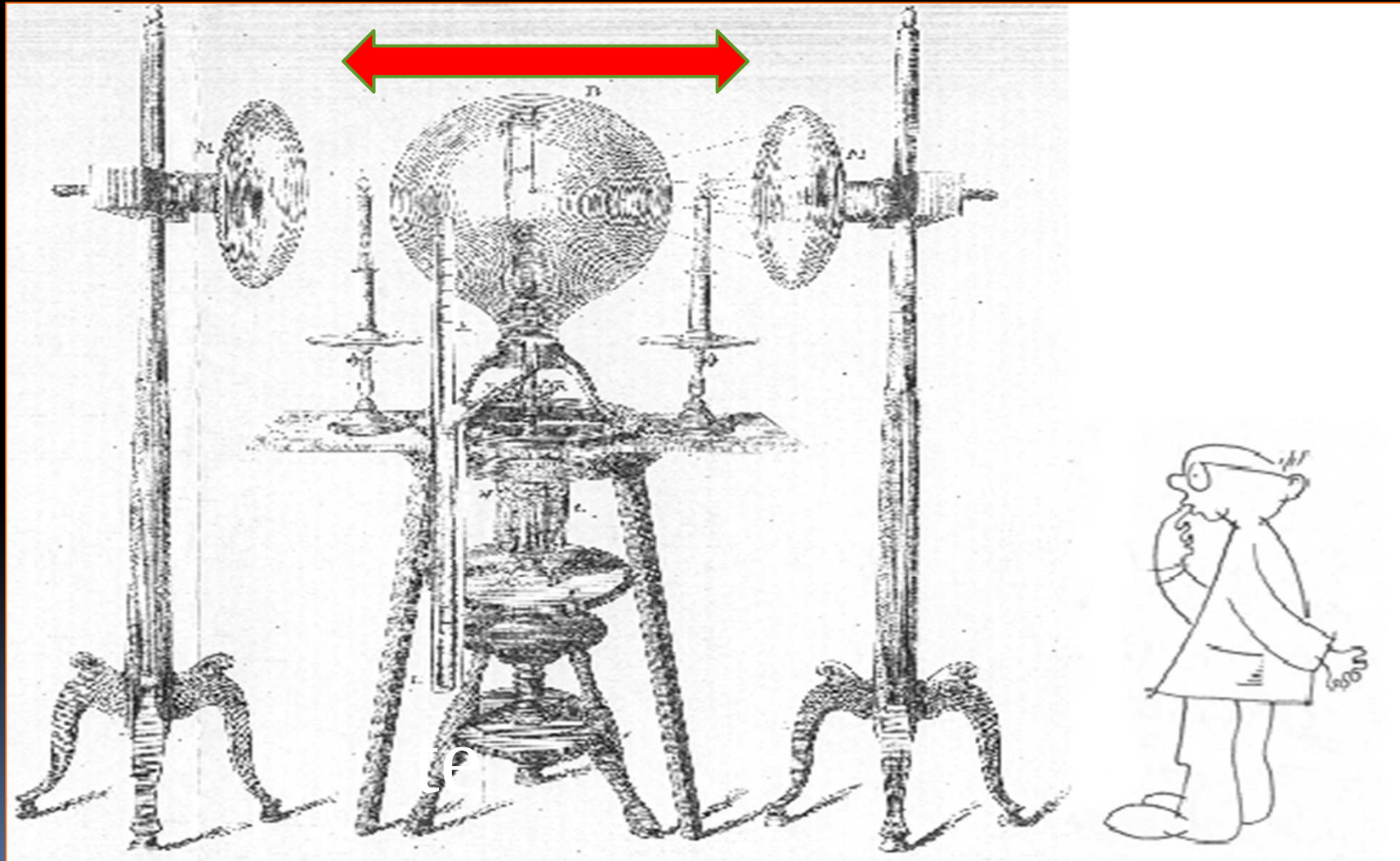


„ „Abychom účinky tepla a
zimy spatřili světle, sluší
se vzíti předmět viditelný i
sluší se počítrovati změn
jeho, když se ohřeje i
když se zase ochladí, aby
se očitě ukázalo, co teplo
a zima dělají smyslům
pochopitelné“

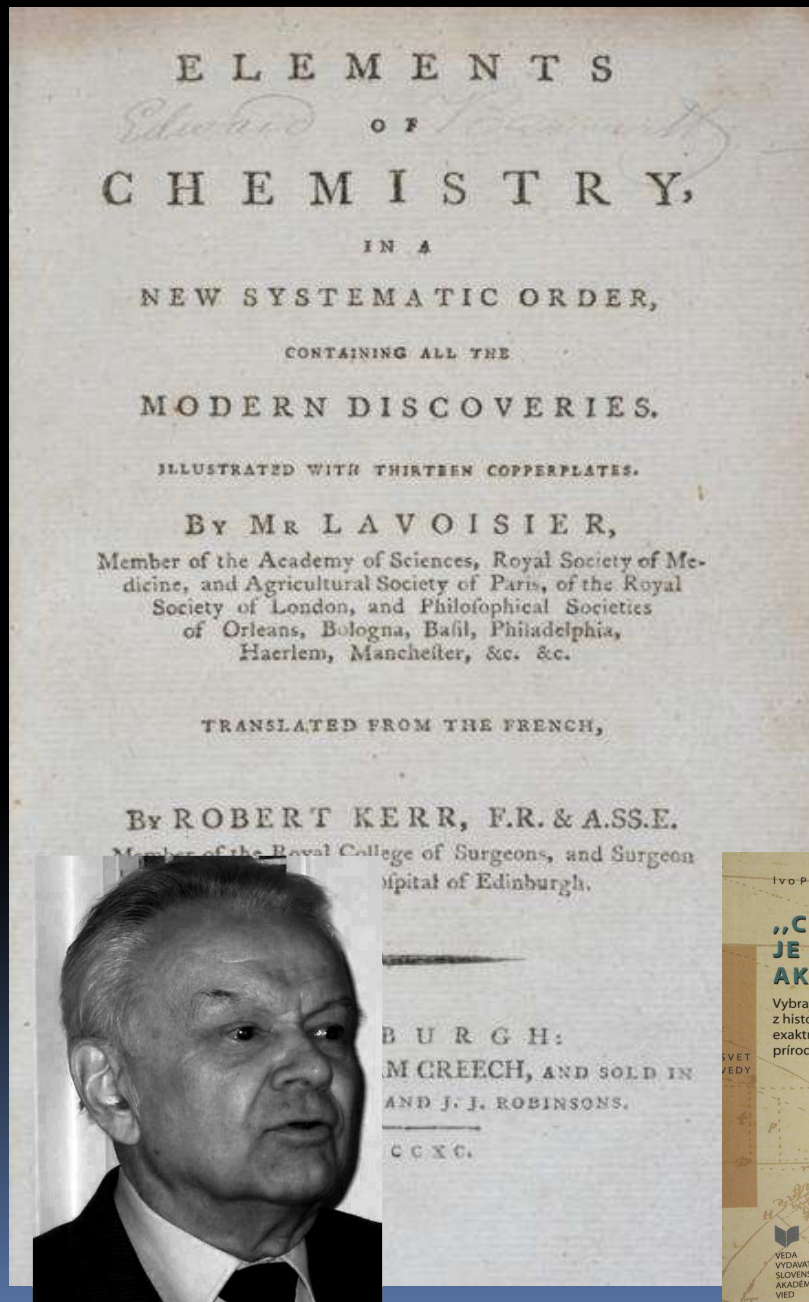
“ introduced „caloric“

Poincaré 1790

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



Heat as an element



ELEMENTS

TABLE OF SIMPLE SUBSTANCES.

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

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

Oxydable and Acidifiable simple Substances not Metallic.

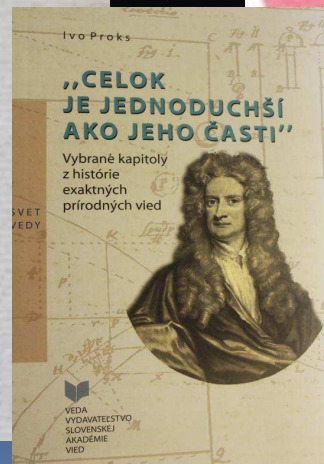
New Names.	Correspondent old names.
Sulphur	The same names.
Phosphorus	
Carbon	
Mercuric radical	Still unknown.
Fluoric radical	
Boric radical	

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.
Tungstina	Tungstina.
Zinc	Zinc.

Soluble simple Earthy Substances.

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



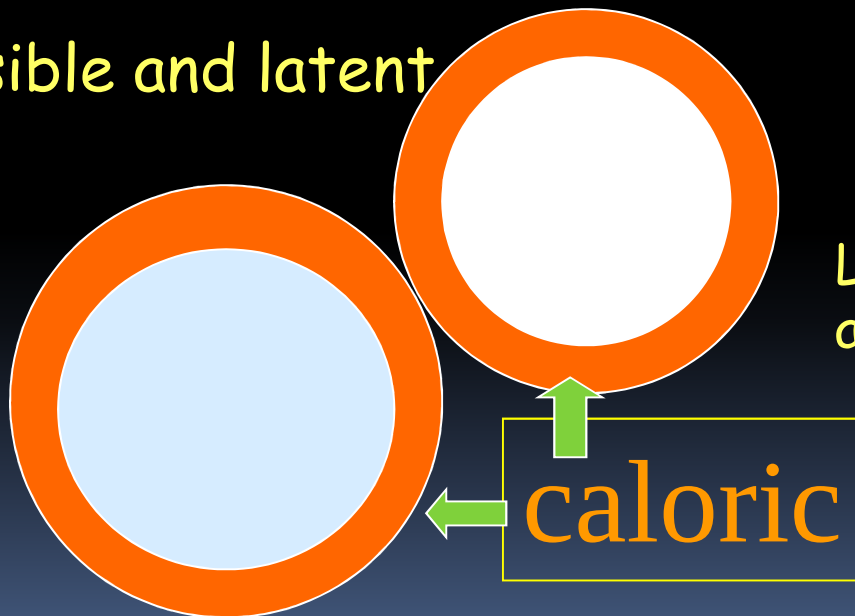
Reneissance :

phlogiston-fuel- palivina
caloricum-medium-teplík

▪ Becher, Stahl → phlogiston (terra pinquis)

Metal = CALX + phlogiston

Sensible and latent
heat



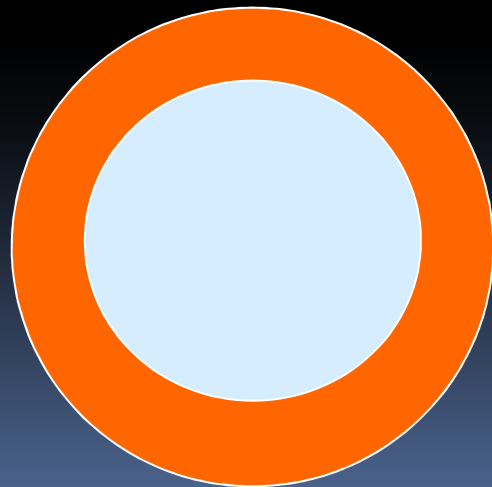
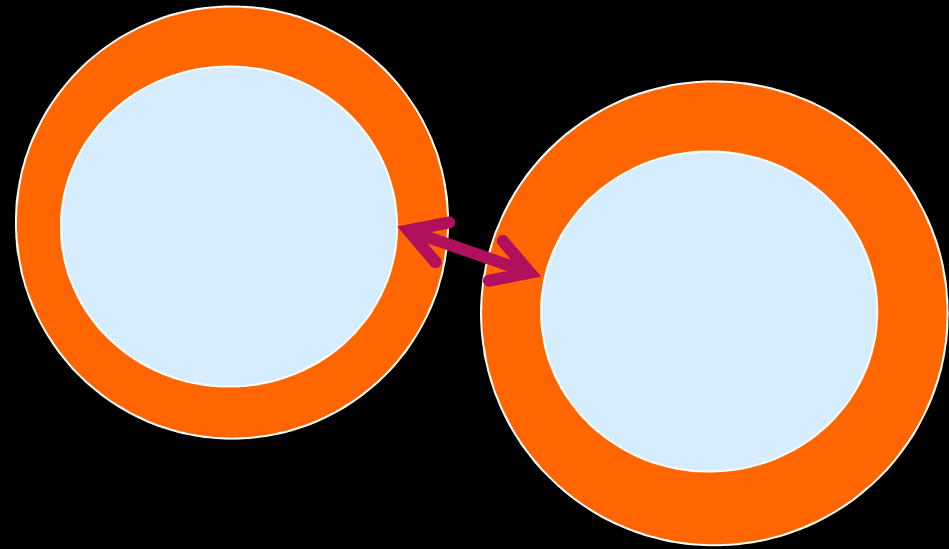
Logarithmic dependence between
amount (quantity) and intensity

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

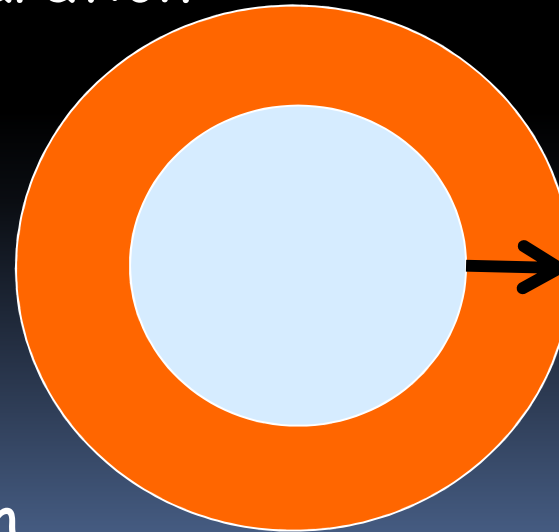
In order to stay away from a total gravitational collision, which would produce a single homogeneous mass, the opposing force was considered to be the '*self-repulsive caloric*'. Such an early '*fluid*' hypothesis became important in the formulation of modern laws and was common to the way of thinking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



phase separation

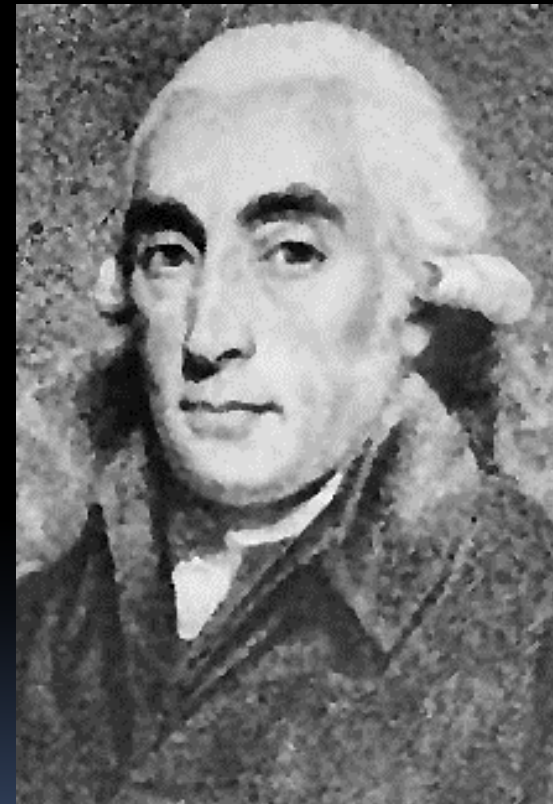
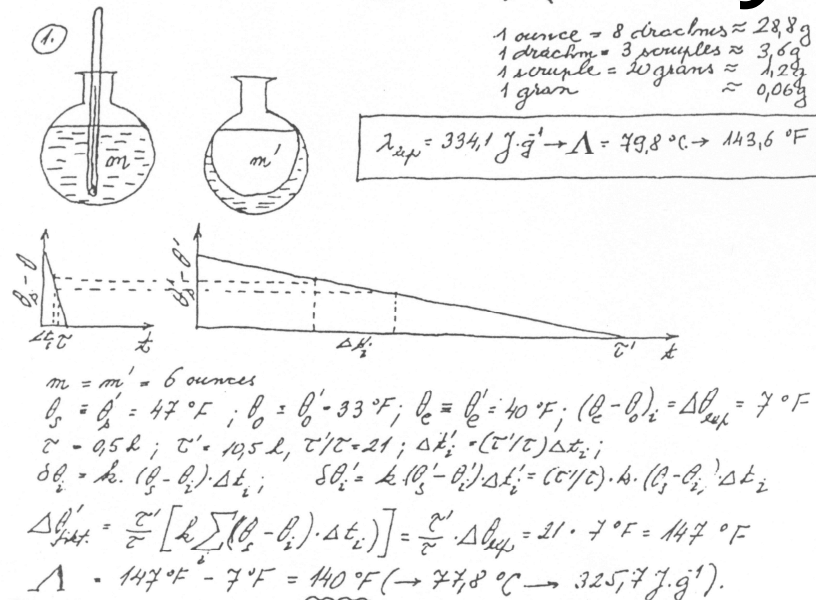


dilatation



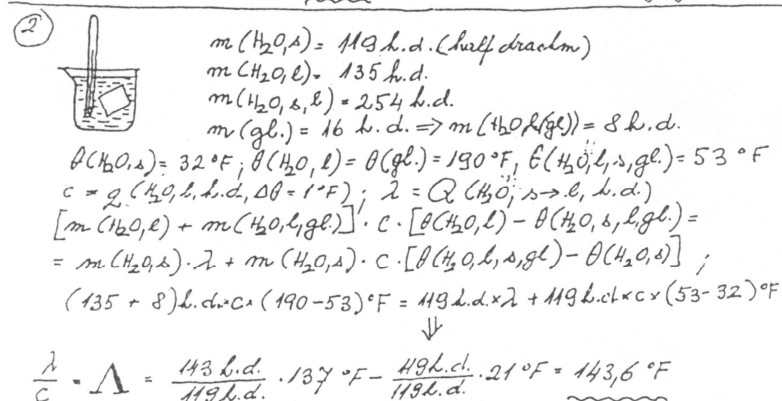
Distinguishing specific heat, latent heat and temperature: launching thermometry

and calorimetry



J. Black (1728-1799)

J. Irvine (1733-1791)



TEPLO, TEPLOTA, TEPLOZPYT



Kabaret
Majora
Kopřivy:
**Mrázospýtem
k teplozpytu**



Temperature	Heat
Temperatur	Wärme
Température	chaleur

Teplota	teplo
Temperatura	ciepło
Температура	тепло

Θερμοκρασία θερμότητα

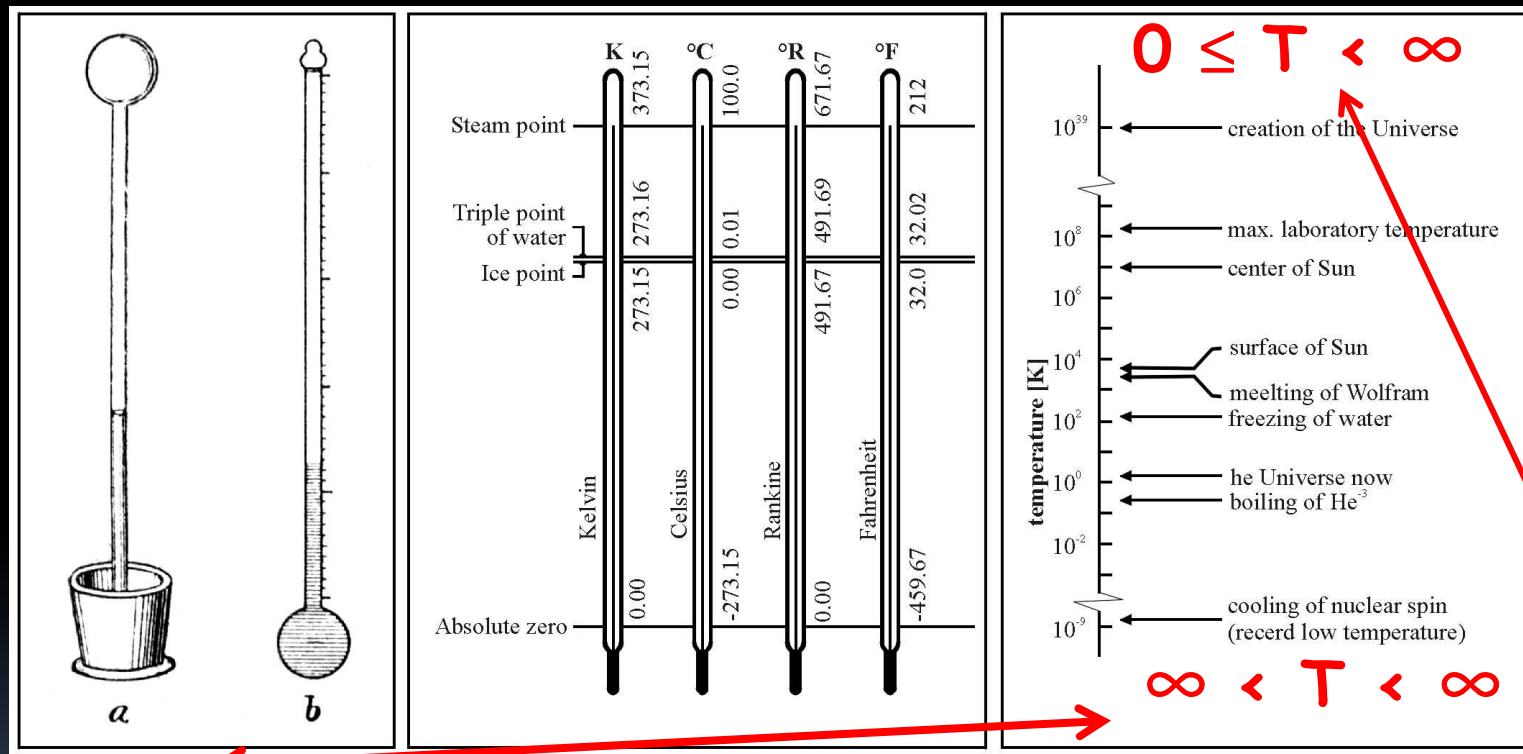
Teplo – **teplozpyt** - calorimetry

тепла исследование

Temperature scale & calibration



Čím horší pivo,
tím dříve
zmrzne



Newton ($T=12 \{2^{\times-1}\}$, 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 ??



Similarity of Newton's law of gravitation

$$F = m a$$

ensue many other principles

Law of heat transfer (Fourier) $q = \lambda \nabla T$

Law of diffusion (Fick) $J = D \nabla c$

Law of electric flow (Ohm) $I = r \nabla u$

Law of thermal inertia $T_i = C_p d^2 T / dt^2$

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?



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



m

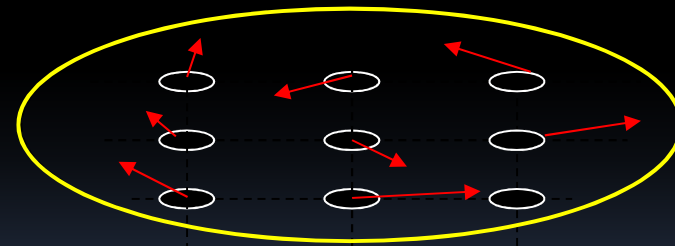


Any matter transport desires definite time lag

Fluid-like transfer

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

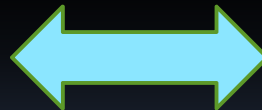
C_p



Heat sink within the sample thermal capacity

Gravity on a micro-level

similarity



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

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

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

⇓

$$(T_h - T_c) = (T_{h0} - T_c) \exp (- (t - t_0)/\tau)$$

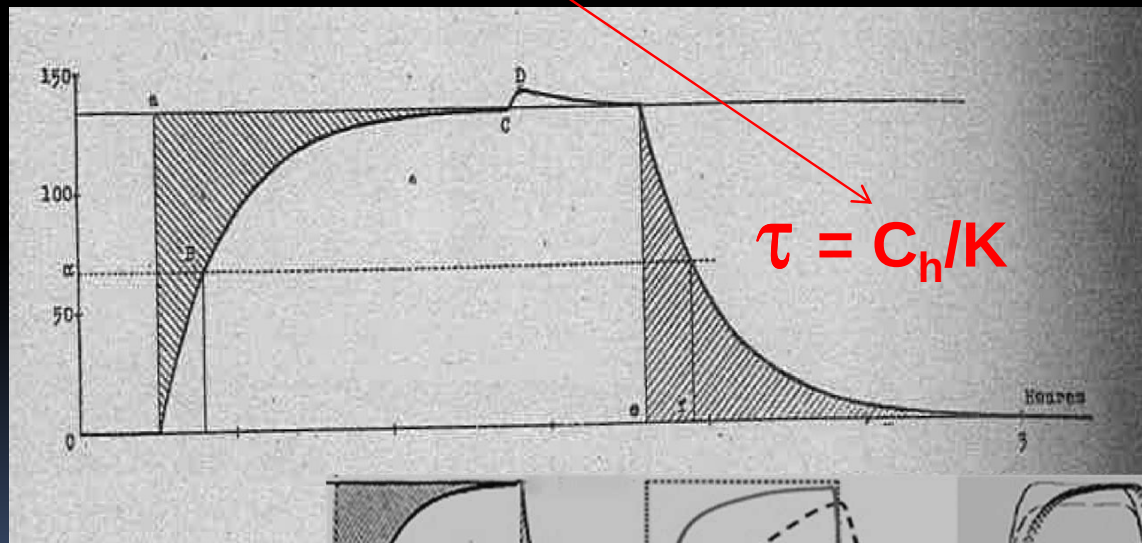
where T_{h0} is the *initial temperature* of hot body and

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

Latter applied by Tian in his basic calorimetric equation

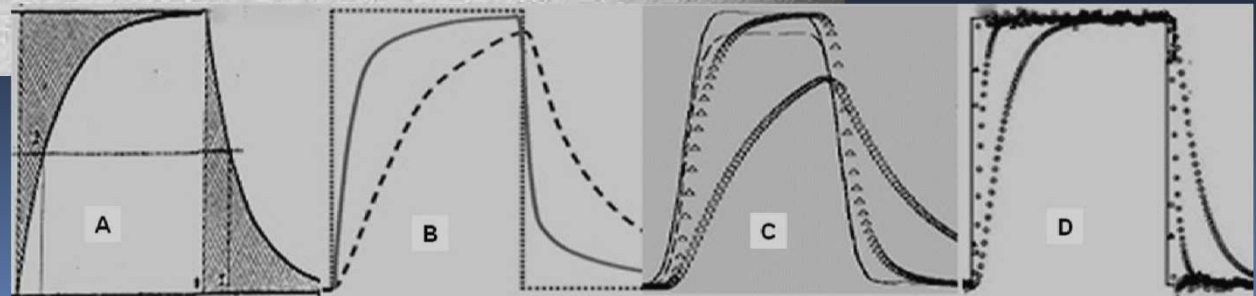
History 1933

⇒



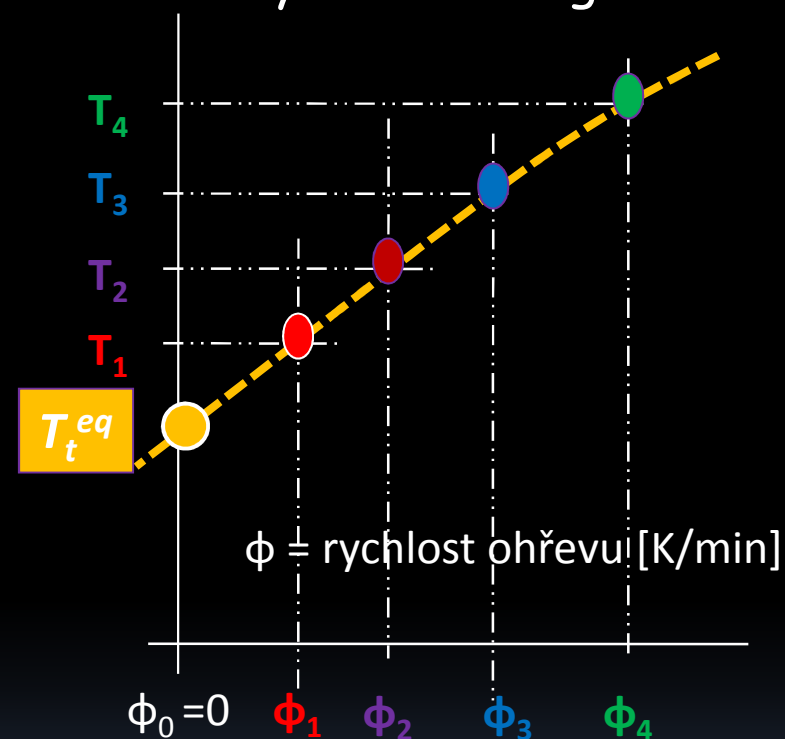
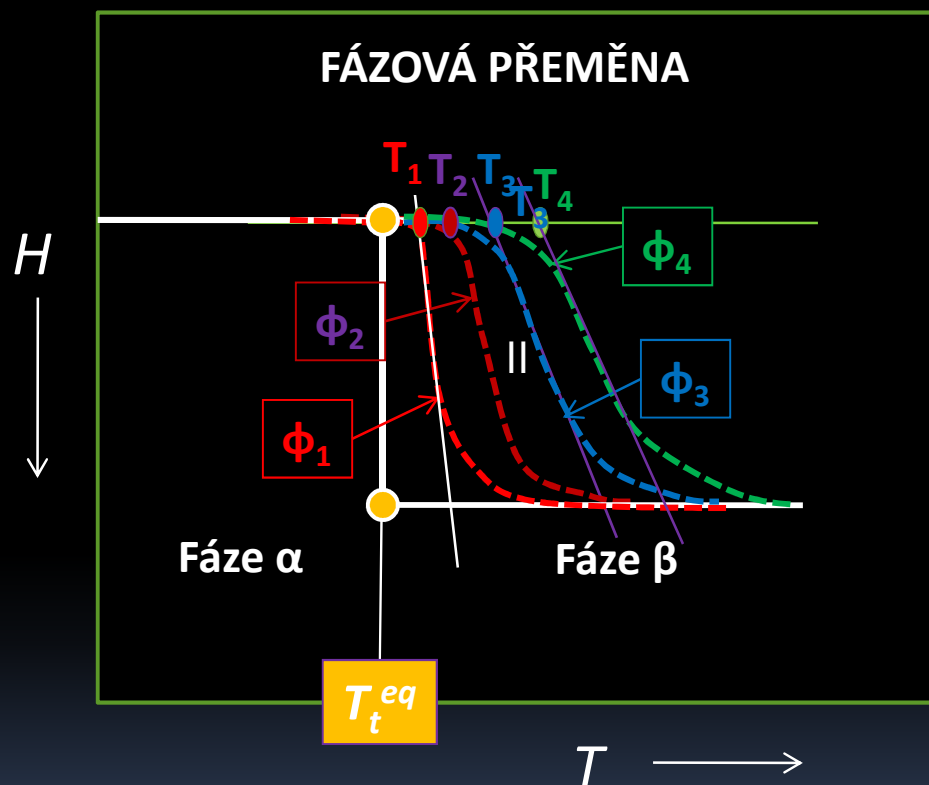
$$\tau = C_h/K$$

Present day ↓



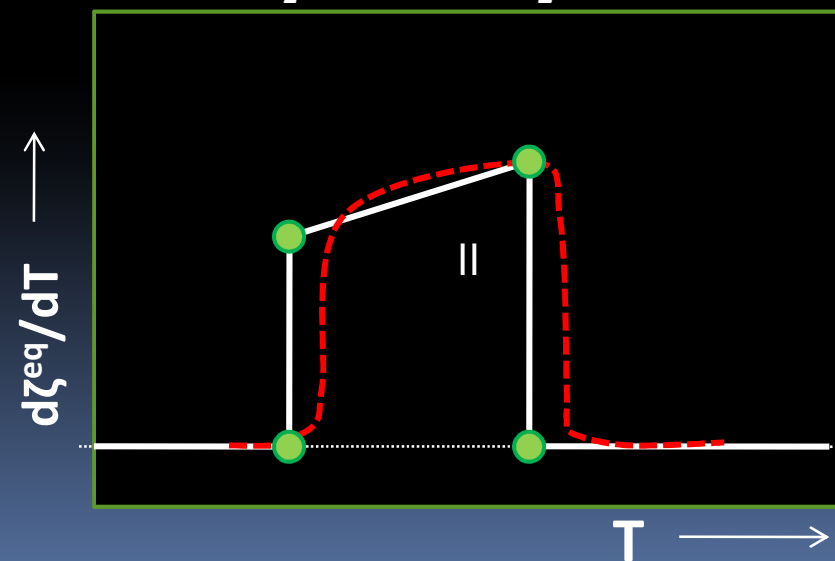
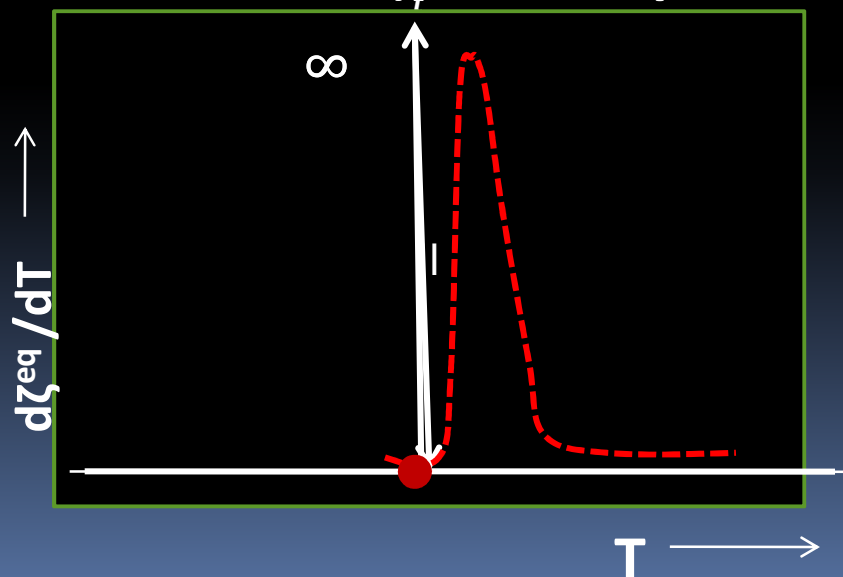
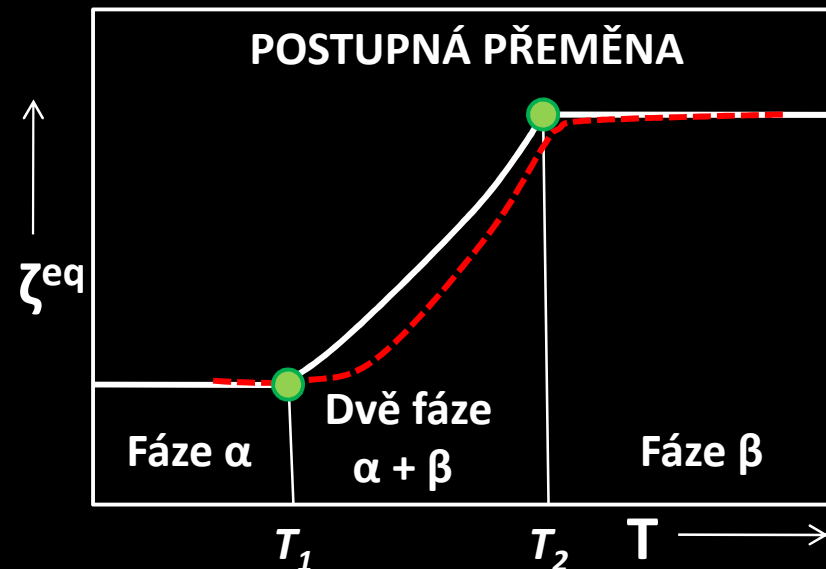
Rovnovážná teplota fázové přeměny: T_t^{eq}

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.

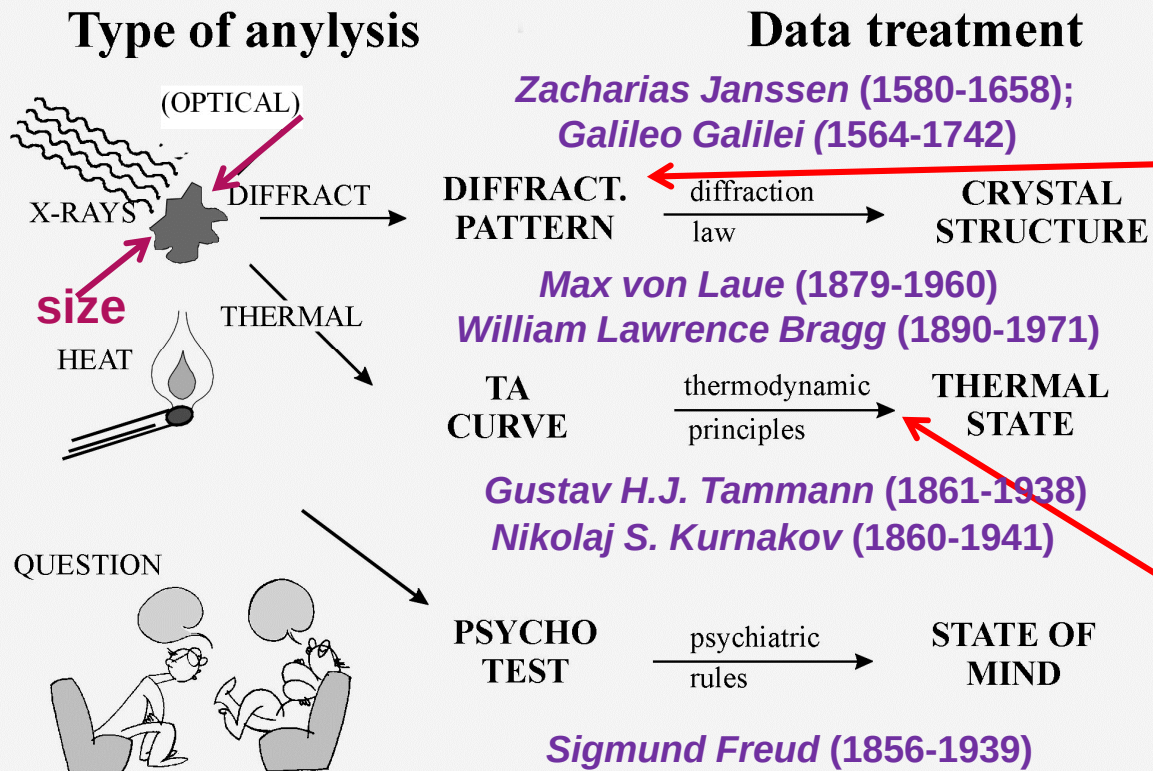
Fázové přeměny a teplotní derivace entalpie



ANALYSIS analogy

SEARCH FOR INFORMATION

Information transducer



Instrumental interface

Evaluation procedure

optical ~ 600 nm
(set-up of crystals)

Nondestructive

X-ray ~ 0.5 nm
(ordering of atoms)

Destructive

Spectroscopic methods

X-ray

Identity
“fingerprint”

Position
Symmetry
Quality

Quantity
Intensity
Area

Shape
Broadening
Crystal size

Heat transfer methods

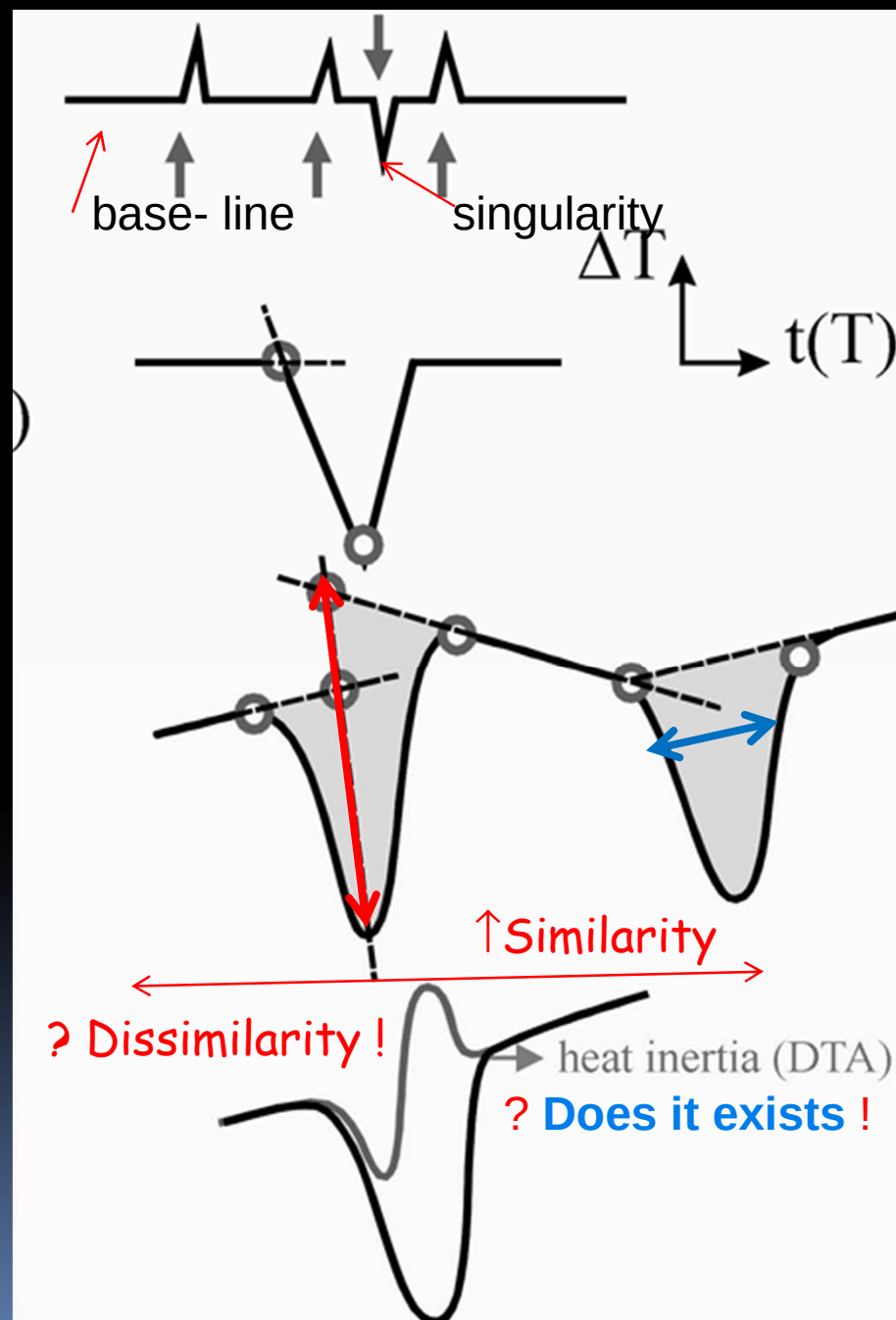
DTA

Identity
“fingerprint”

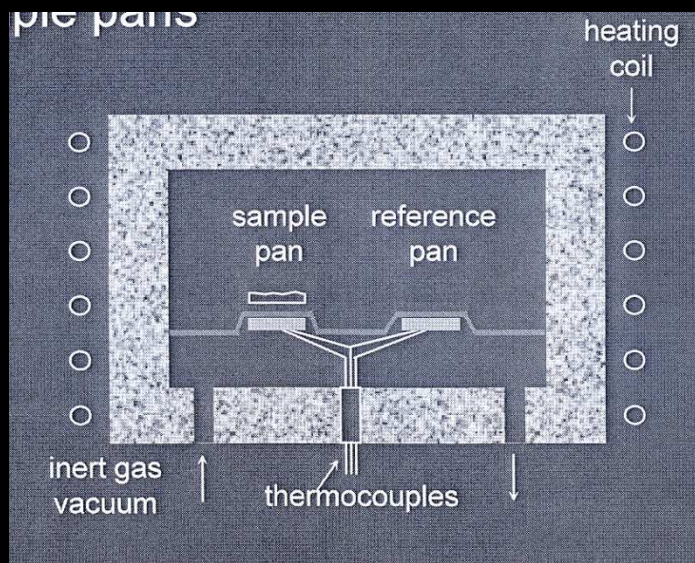
Position
Uniformity
Quality

Quantity
Size
Area

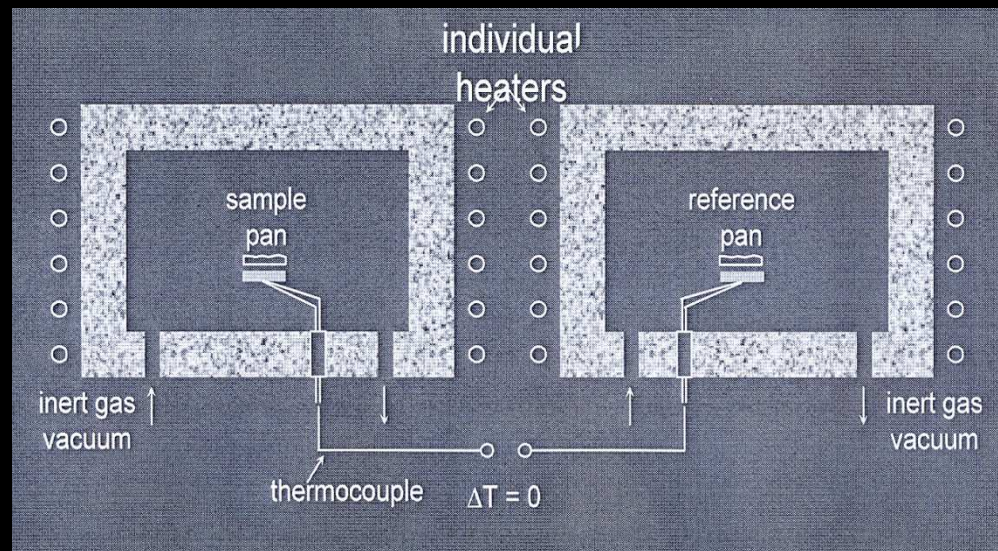
Shape
Structure
Kinetics



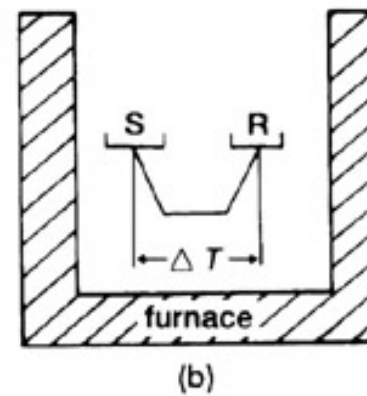
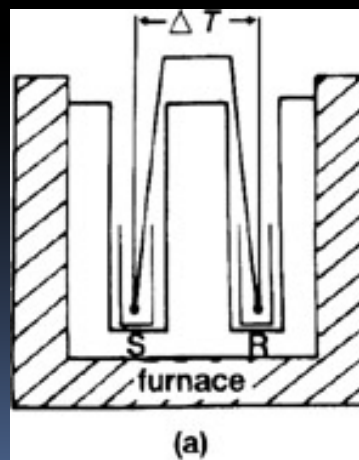
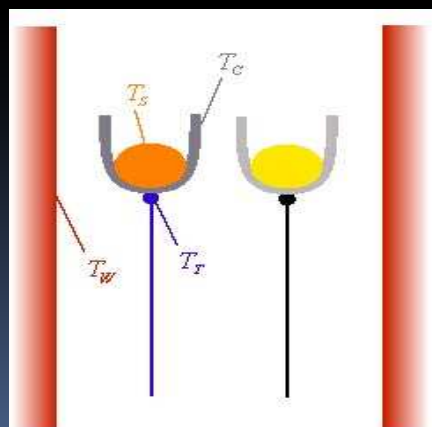
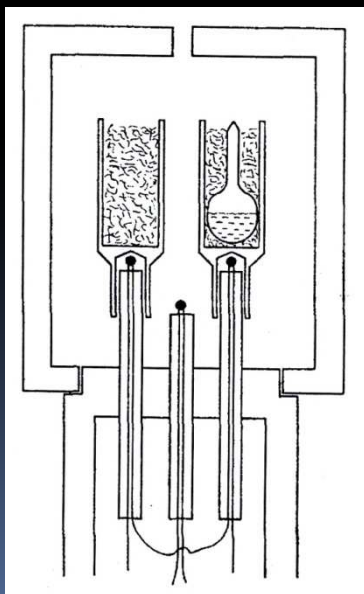
Heat-flux DSC



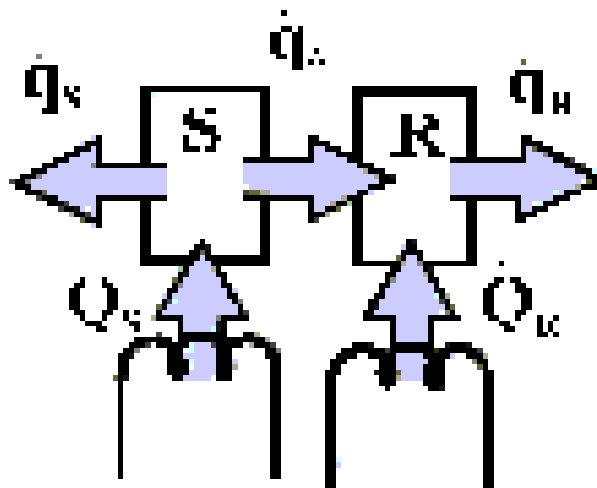
Compensation DSC



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

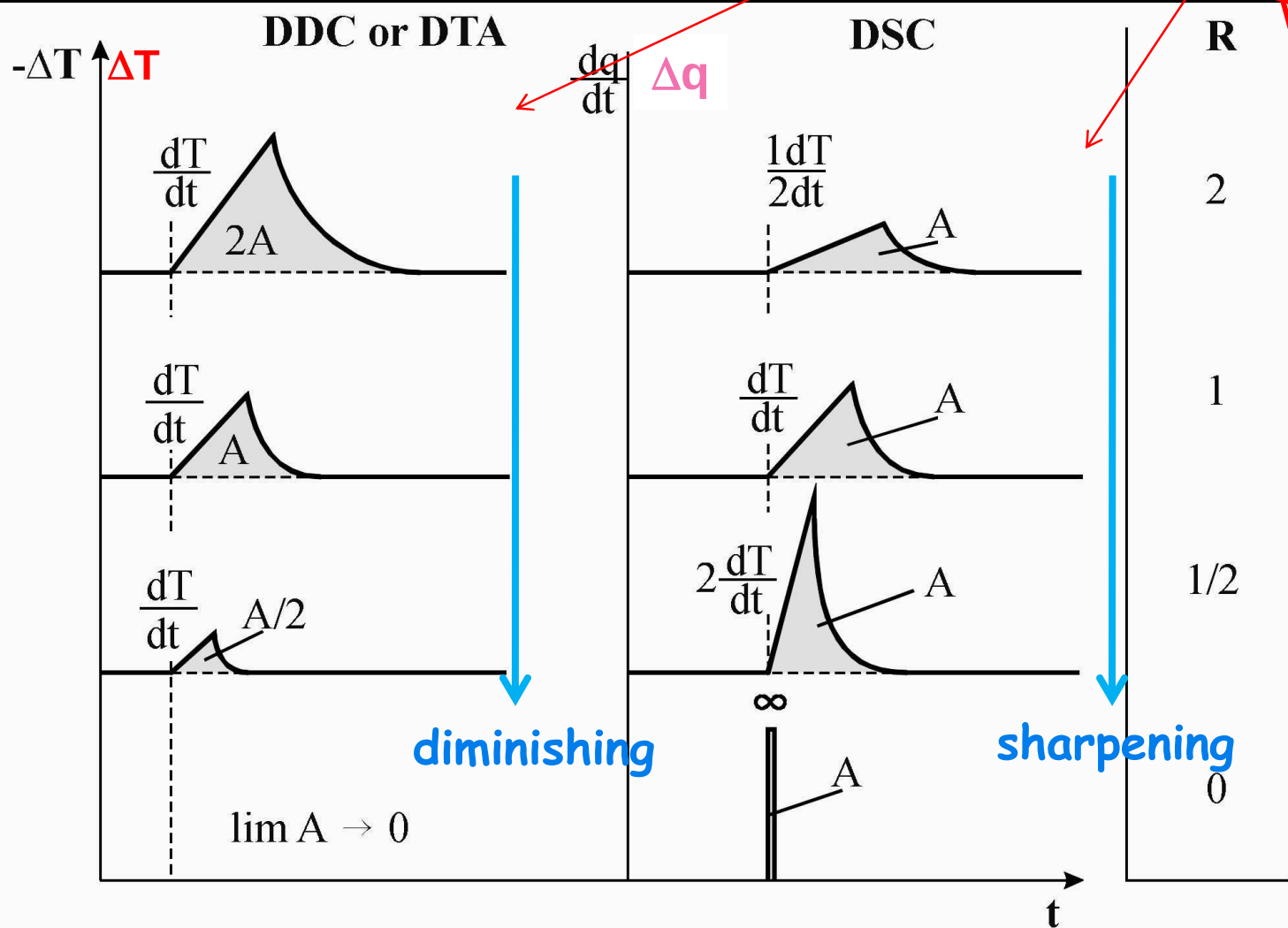
$$(Ts \cong Tr) \text{ and } \Delta T_{DTA} \approx 0$$

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

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

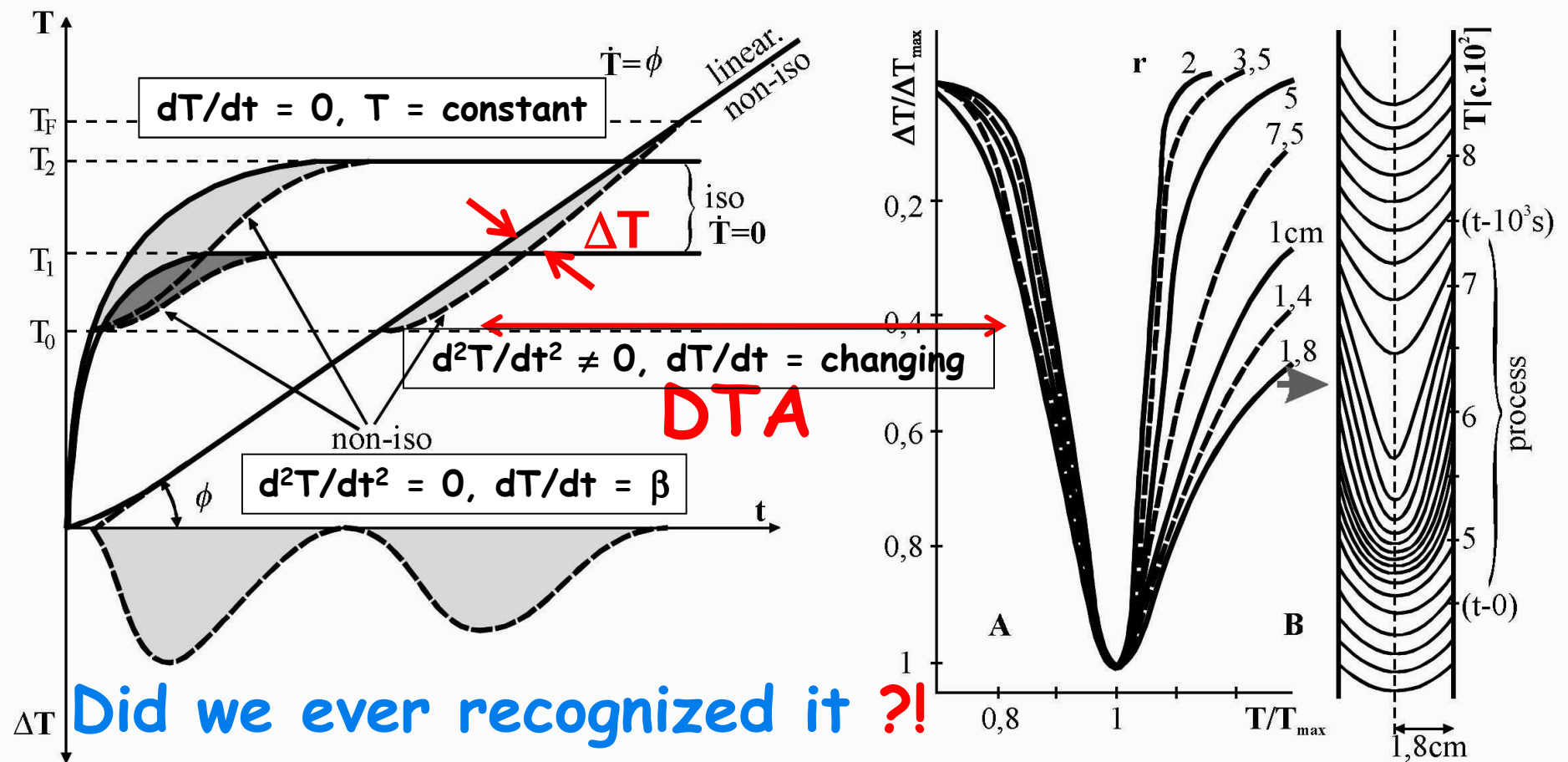
Why are the curves/peak by DTA and DSC different ?

Mutual comparison of the sensitivity of measurements

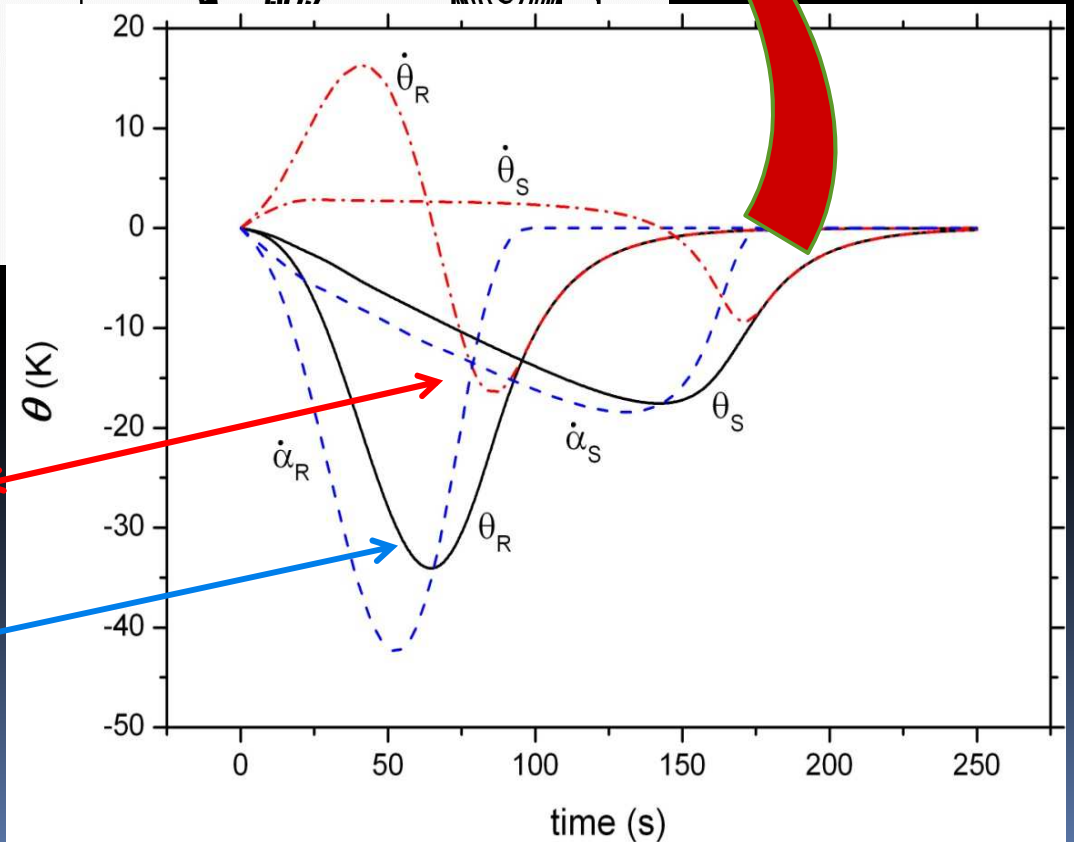
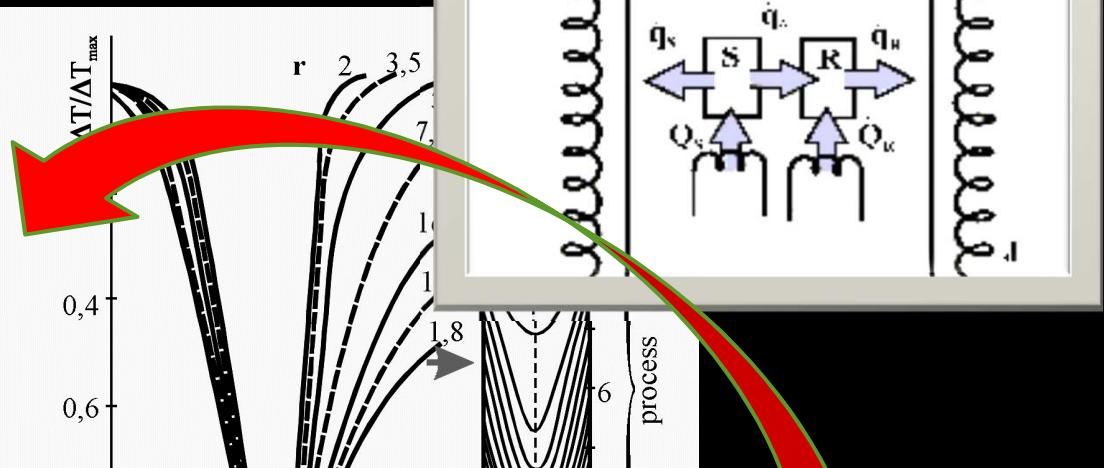
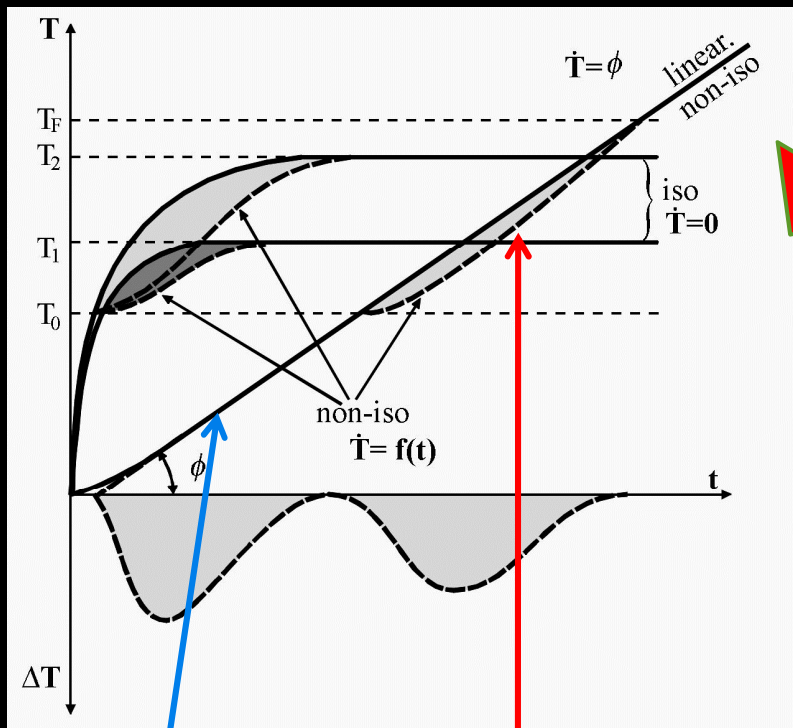


Can we recognize its consequences ?!

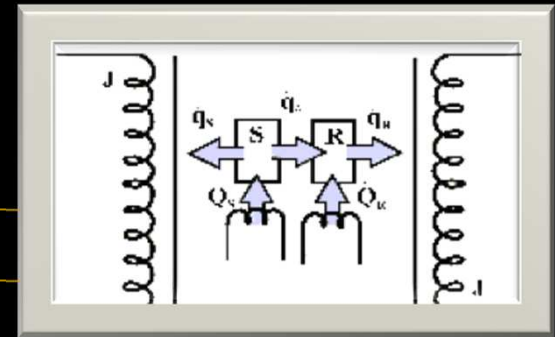
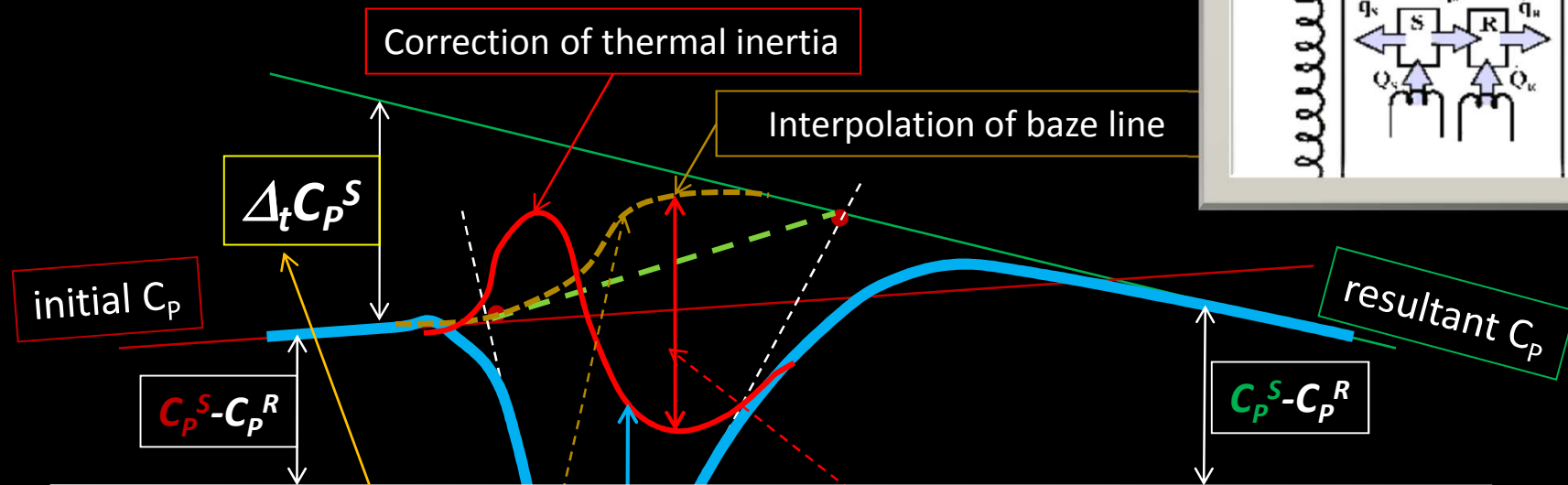
Isothermal and non-isothermal measurements: naturally involves thermal setups-gradients



Holba P, Šesták J. (2015) Heat inertia and its role in thermal analysis. J Thermal Anal Calor, 121:303–307



DTA CURVE



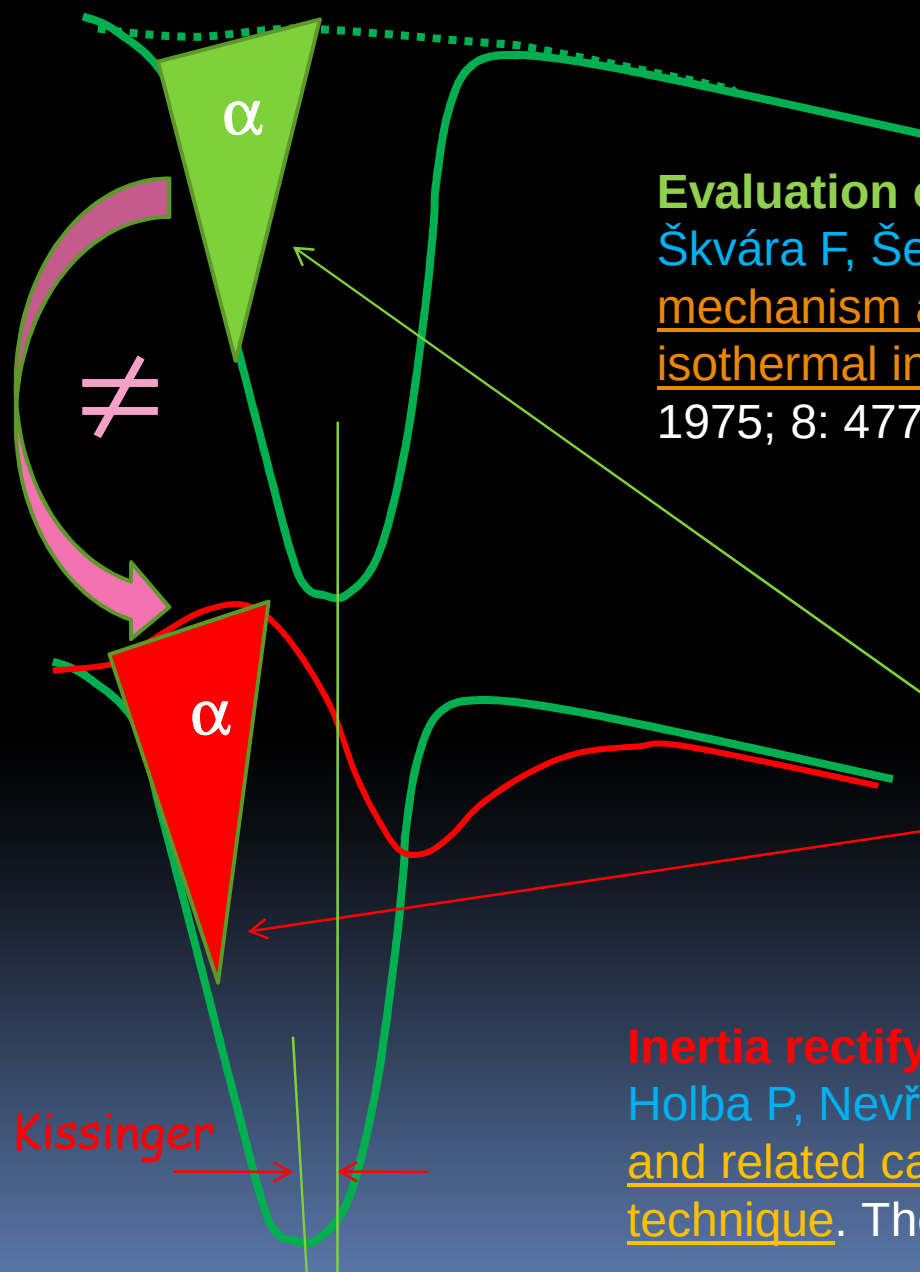
$$\Delta T(t) \cdot K_s(T, \Phi) =$$

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

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

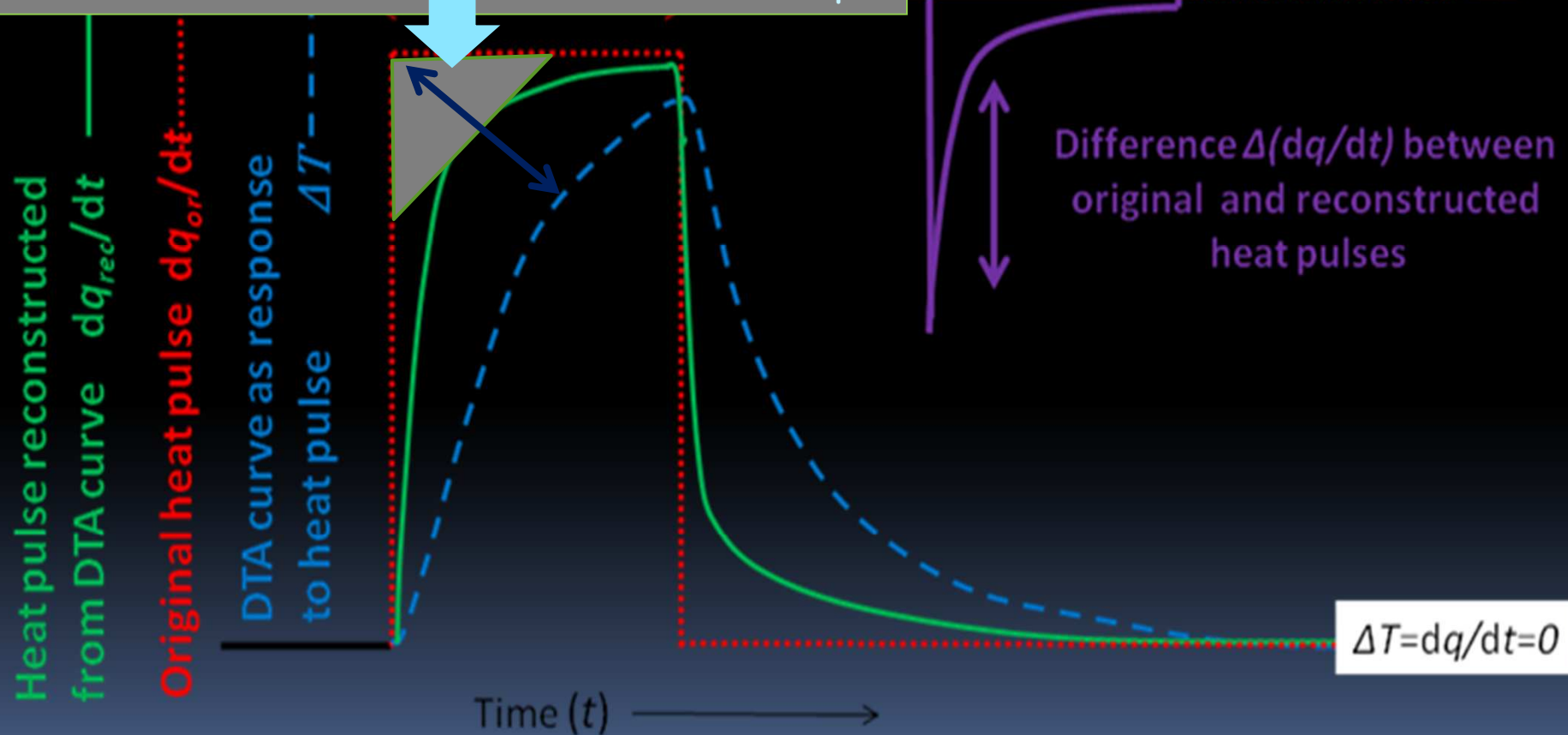
Phase transition of BaCO_3 at 810°C

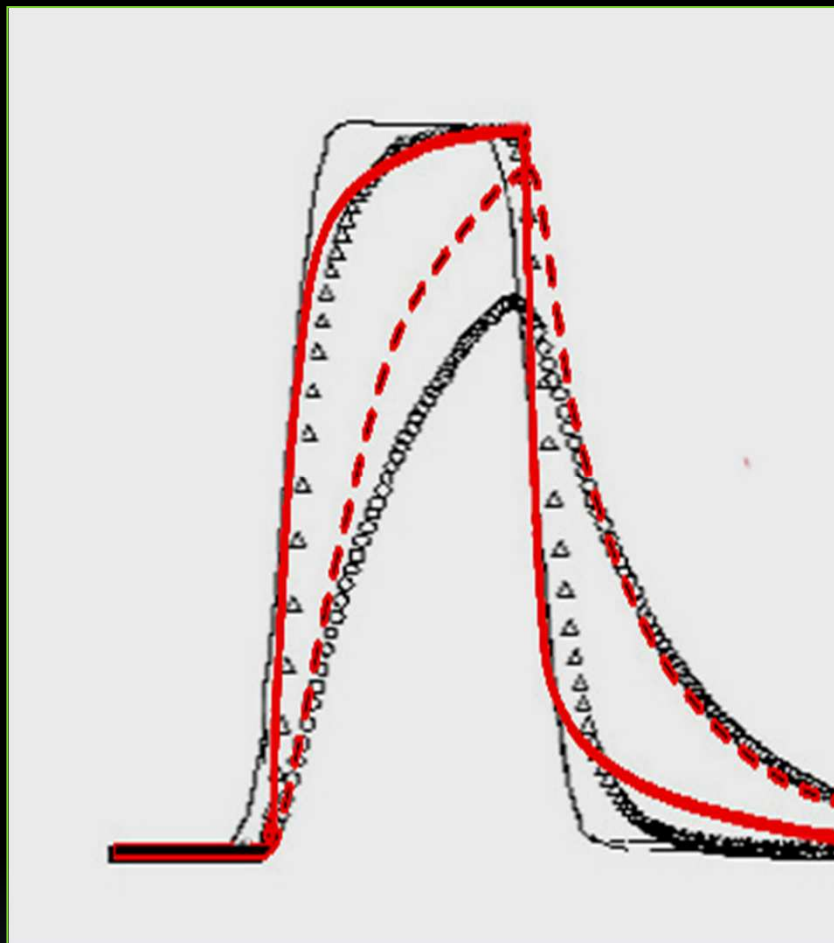
ΔH	E [cal]	mechanism
613	118	A3
617	52	A3

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

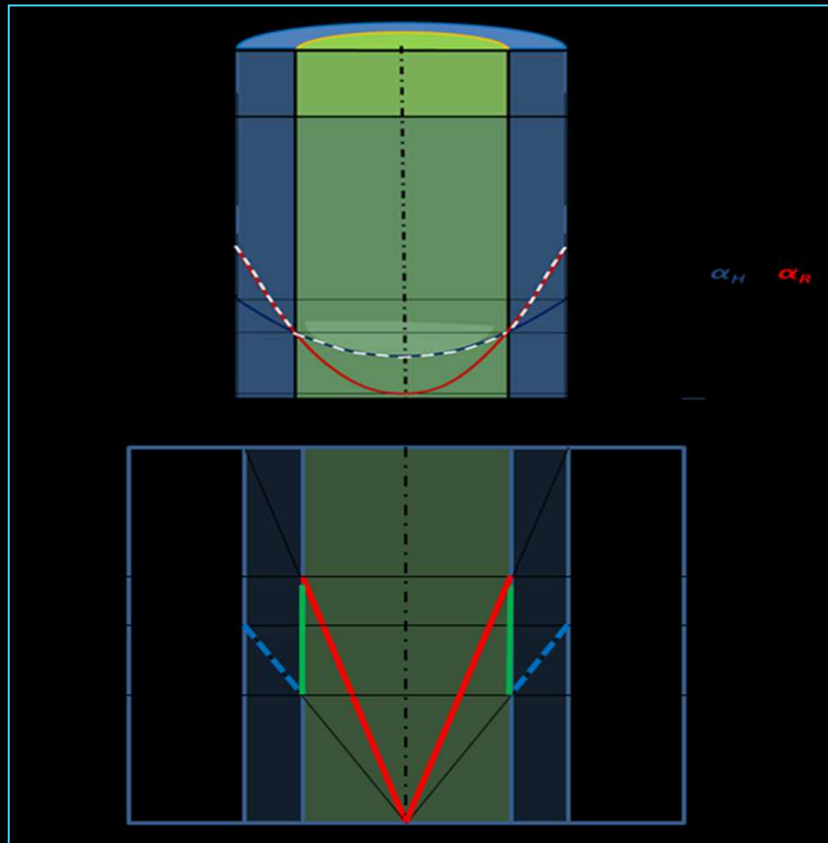




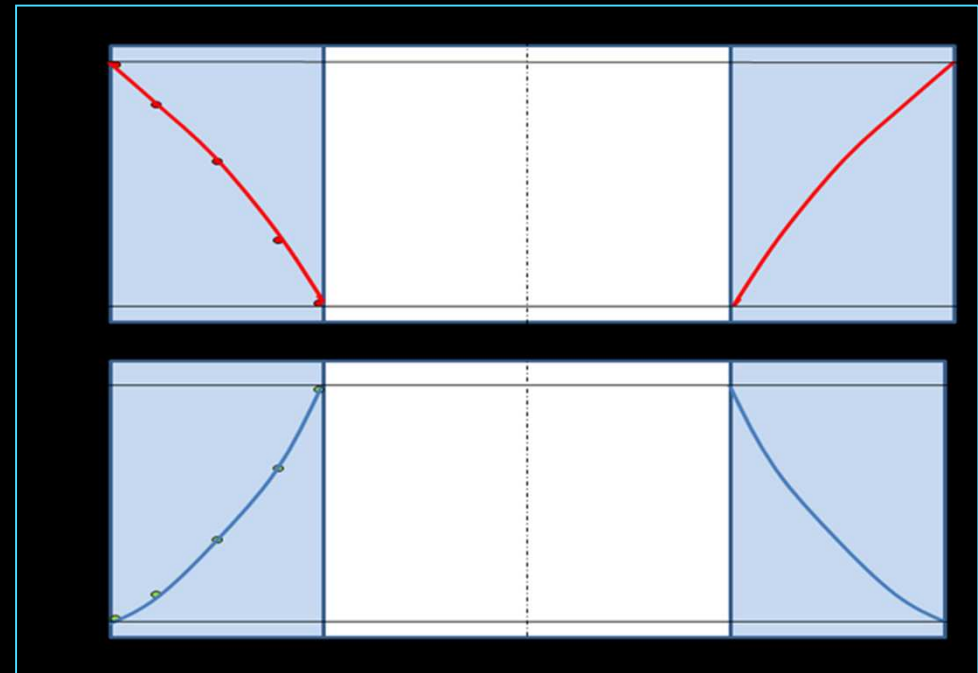
Holba P, Šesták J, Sedmidubský D (2013) **Heat transfer and phase transition at DTA experiments.** Chapter 5 in: Thermal analysis of micro-, nano- and non-crystalline materials (J. Šesták, P. Šimon. Eds), Springer, Berlin, pp. 99-134

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

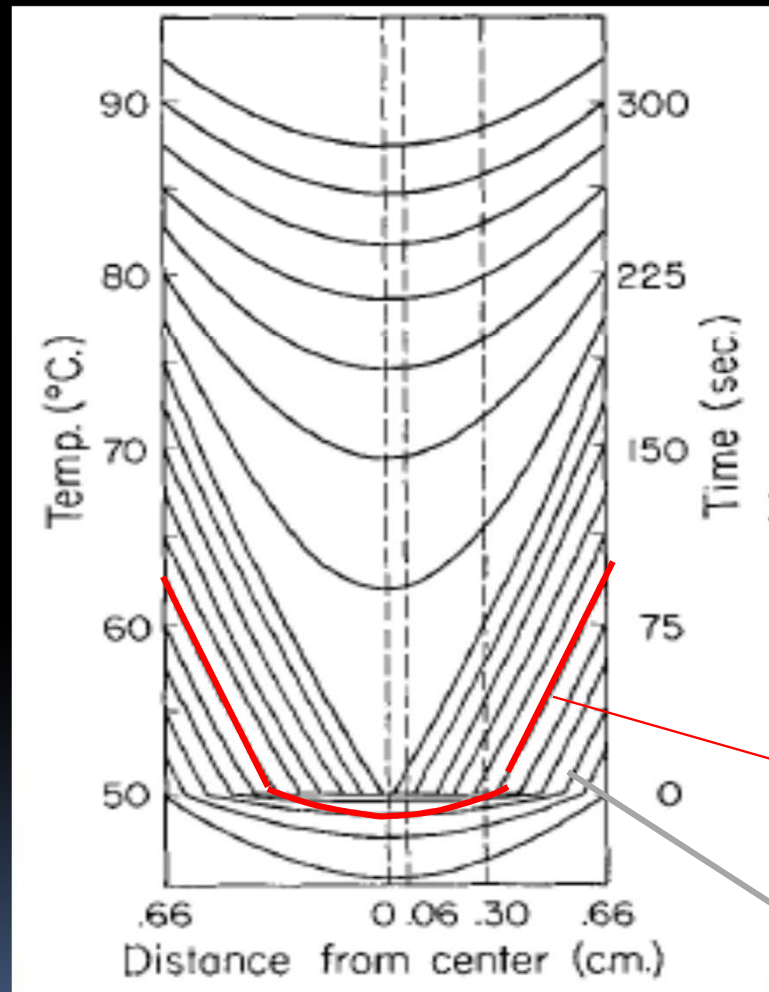


Stabilized temperature profiles $T_R(r)$, $T_H(r)$ and gradient profiles $g_R(r)$, $g_H(r)$ at linear heating ($\Phi_{RE} > 0$) in an infinite cylinder with external radius of holder (jacket) r_H and external radius of reference (core) r_E in the case when the thermal diffusivity of holder material α_H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

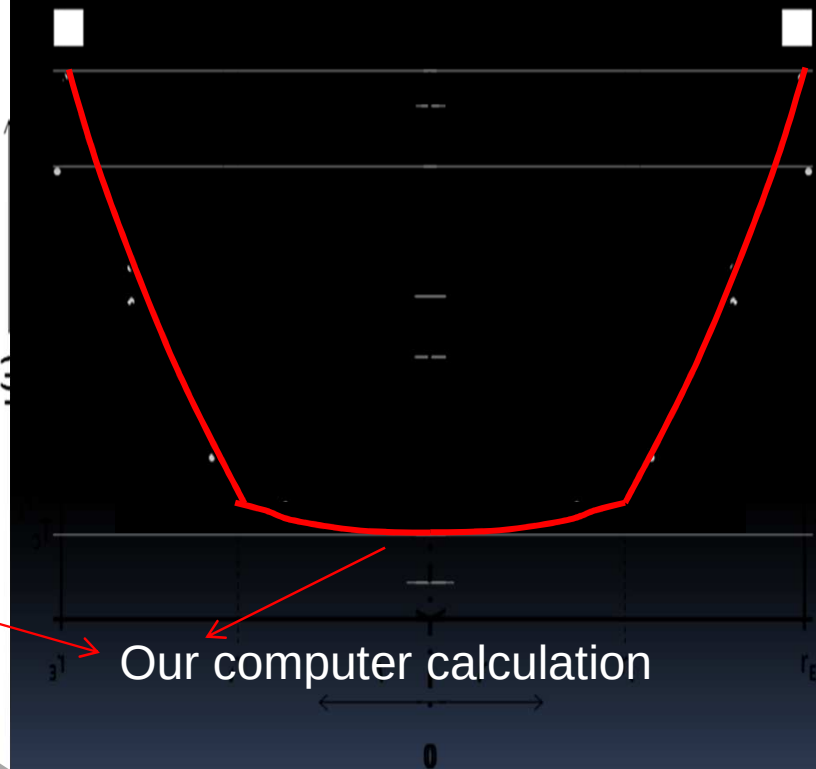


Stationary temperature profile $T_R(r)$ and gradient profile $g_R(r)$ in hollow cylinder with outer radius r_E and inner radius r_I separating outer reservoir with temperature T_E and inner reservoir with temperature T_I

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



1951 data



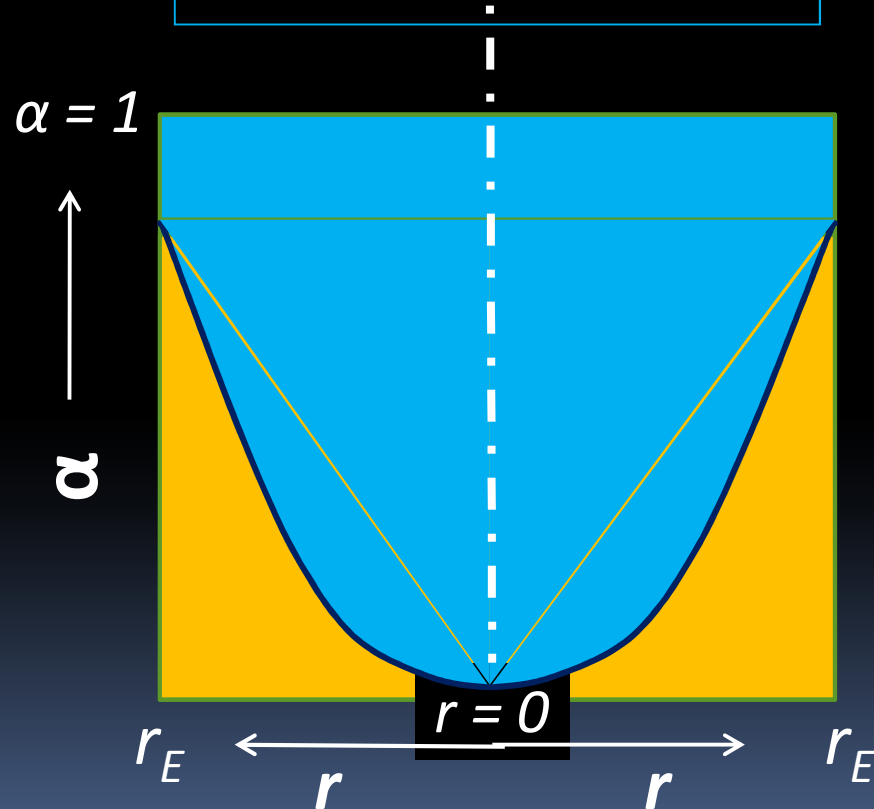
Smyth HT. Temperature Distribution during Mineral Inversion and Its Significance in DTA. J. Amer. Cer. Soc. 1951; 34: 221-224.

Kinetic models of a phase transition

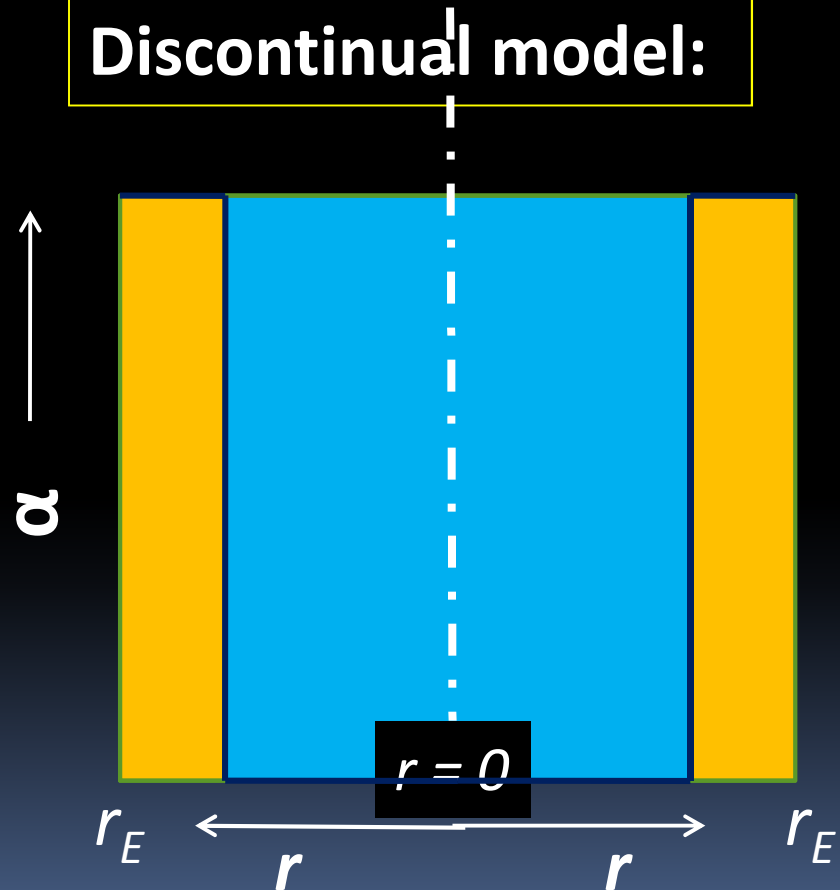
(initial)

(final)

Continual model:



Discontinual model:



Courtesy by Pavel Holba

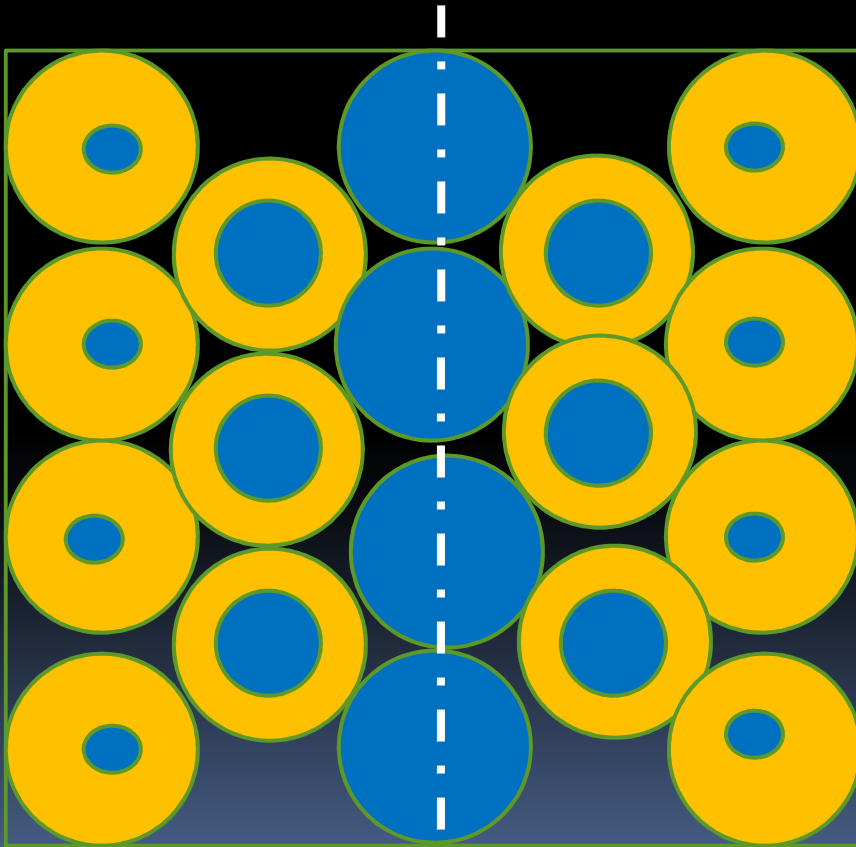
Variants of kinetic models of a phase transition

(initial)

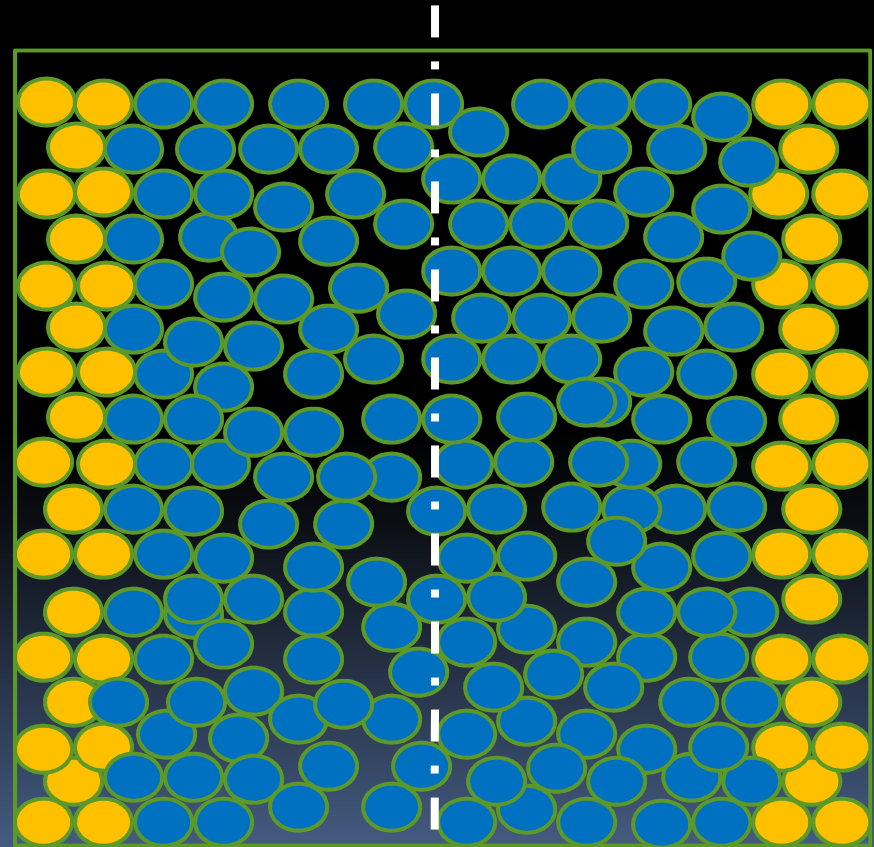
&

(final)

continual model:



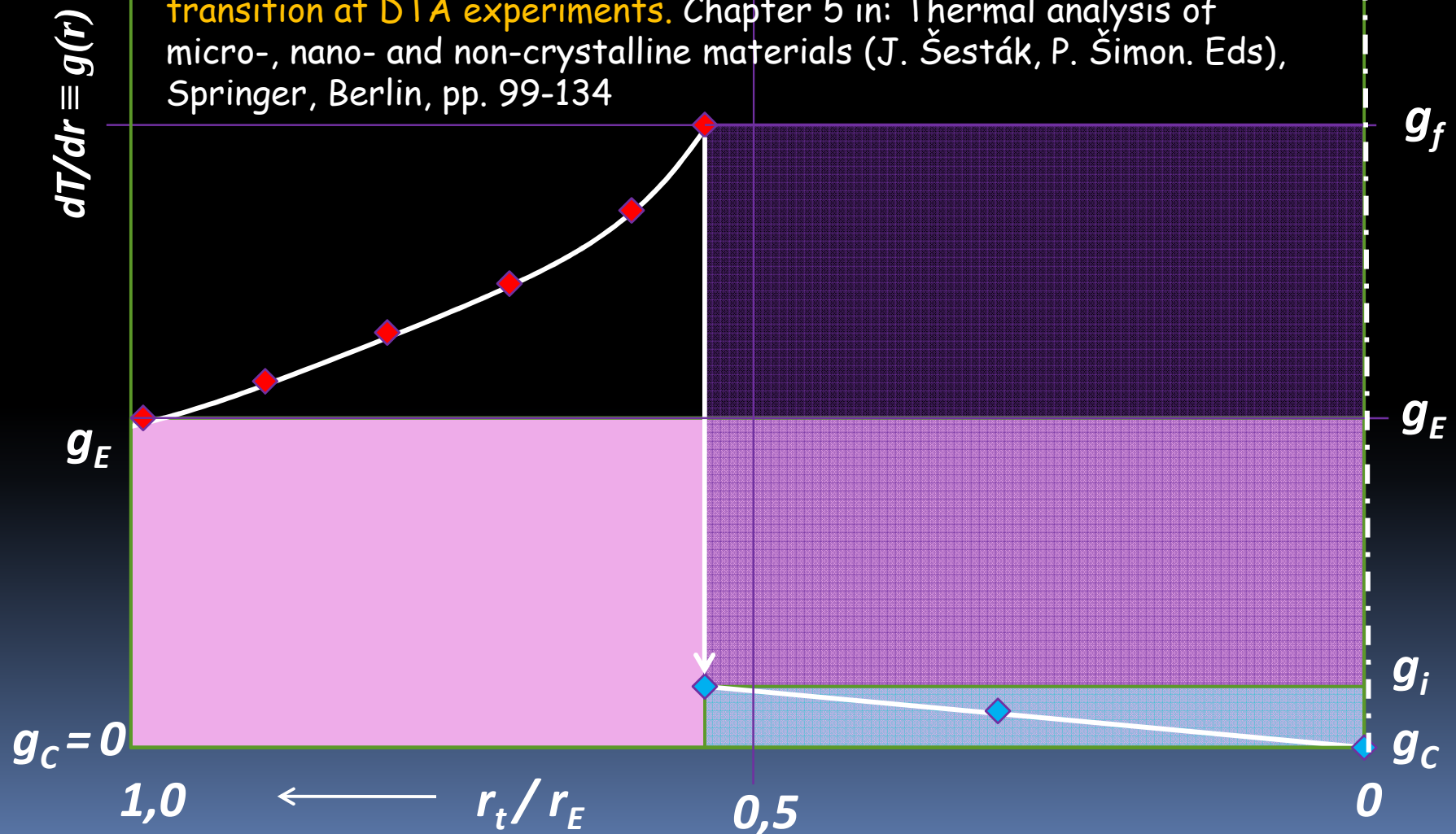
Discontinual model:



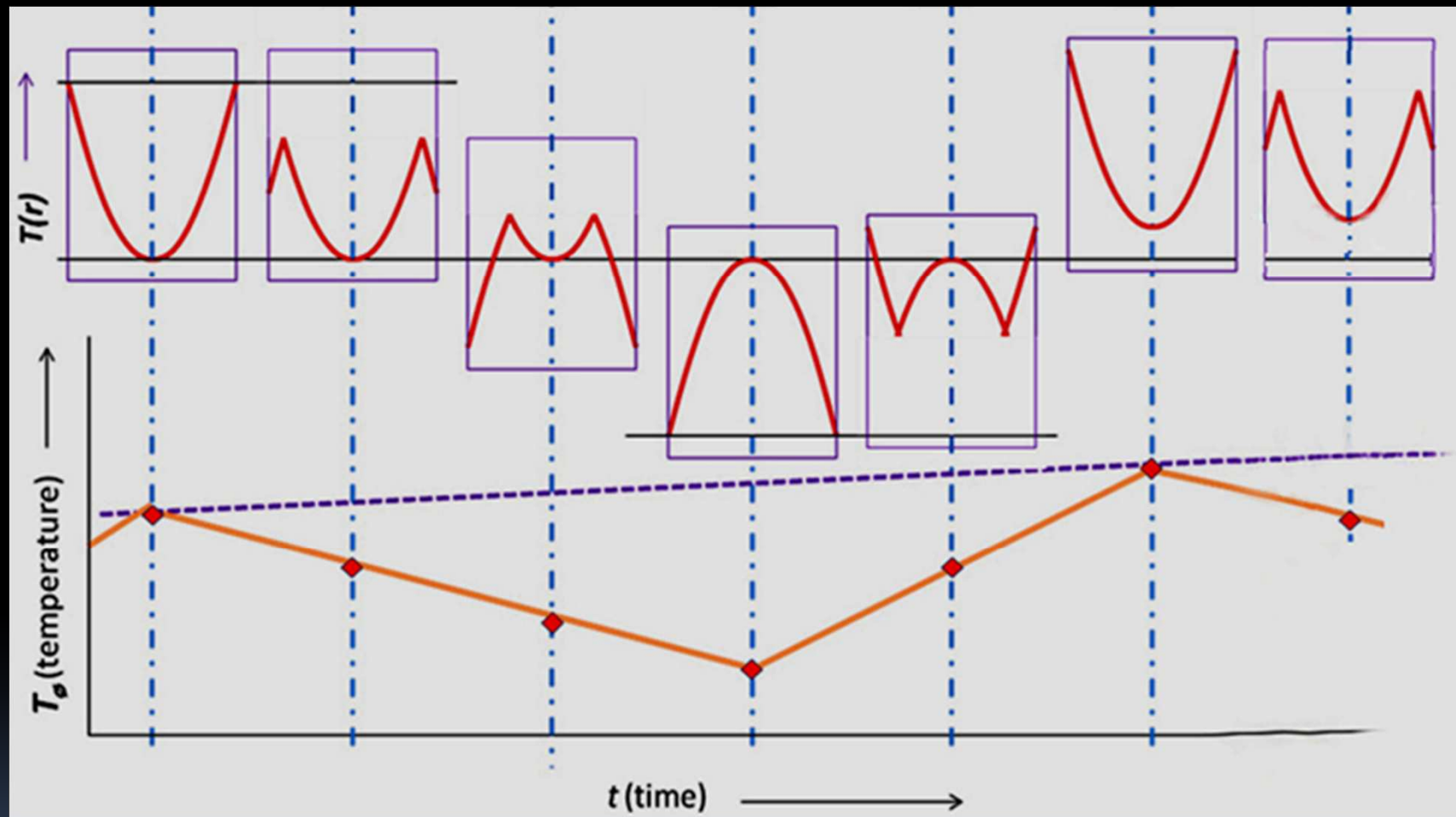
Courtesy by Pavel Holba

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



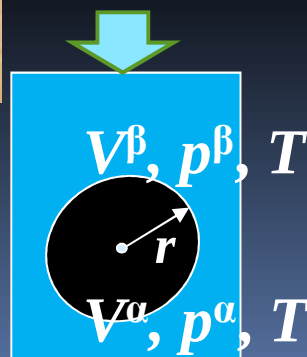
Holba P, Šesták J, Sedmidubský D (2013) **Heat transfer and phase transition at DTA experiments**. Chapter 5 in: Thermal analysis of micro-, nano- and non-crystalline materials (J. Šesták, P. Šimon. Eds), Springer, Berlin, pp. 99-134

What is temperature under extremes?

size matters

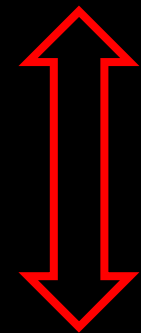


Current study exploring
dimensionality changes,
impact of surface tension



Macro extreme
astrophysics

Extreme
temperature
changes



Micro extreme
nanophysics

Macro-extreme

Relativistic transformations of temperature

Thermodynamics gives ambiguous solutions e.g.

$$T = T_0 \sqrt{1 - v^2/c^2}$$

K. v. Mosengeil (1907)

$$T = T_0 / \sqrt{1 - v^2/c^2}$$

H. Ott (1963)

$$T = T_0$$

P. T. Landsberg (1966)

⇒ One century of controversy in solution of a fundamental problem of relativistic thermal physics

⇒ Our suggestion: relativistic constants, e.g.,

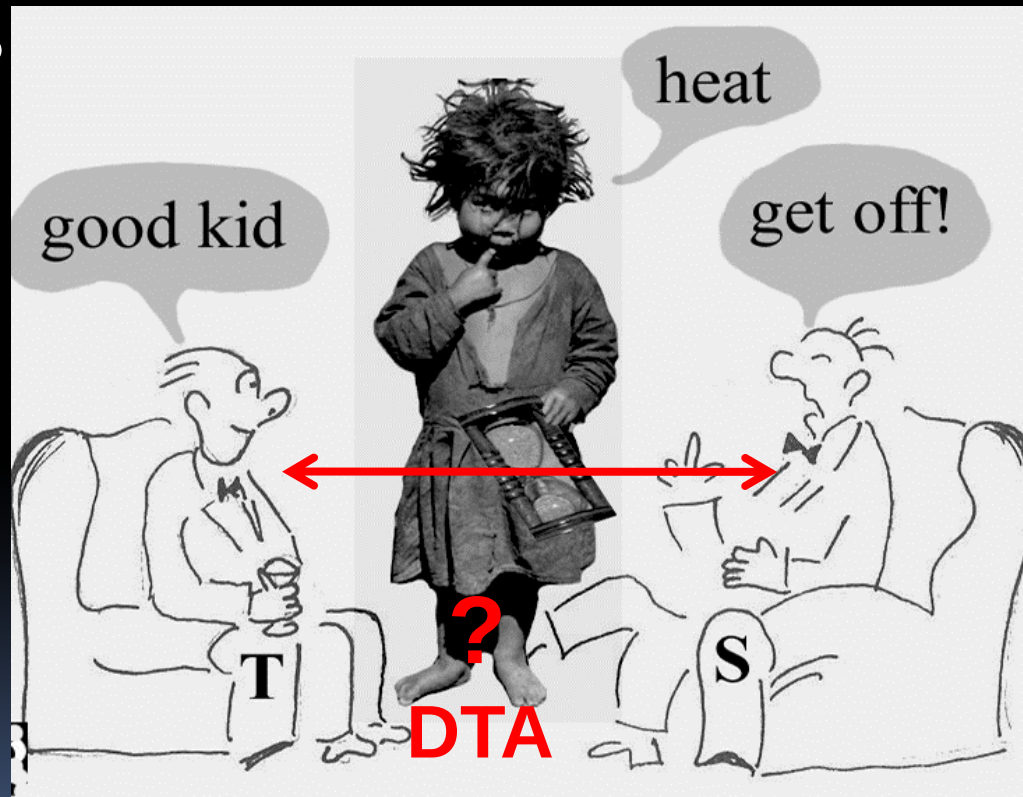
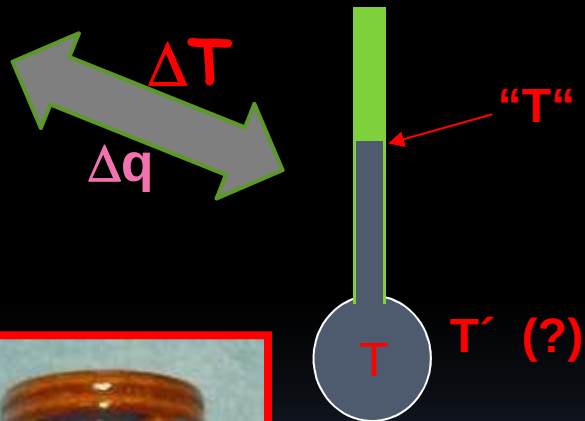
$$\Rightarrow k = k_0 \sqrt{1 - v^2/c^2}, \quad R = R_0 \sqrt{1 - v^2/c^2}$$

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

Ultra-fast processes - what is temperature contrivance of thermodynamics

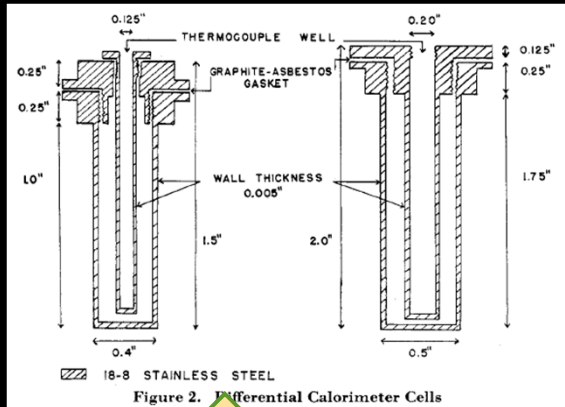
What happens if there
is no time for the system
fast-enough equilibration?

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

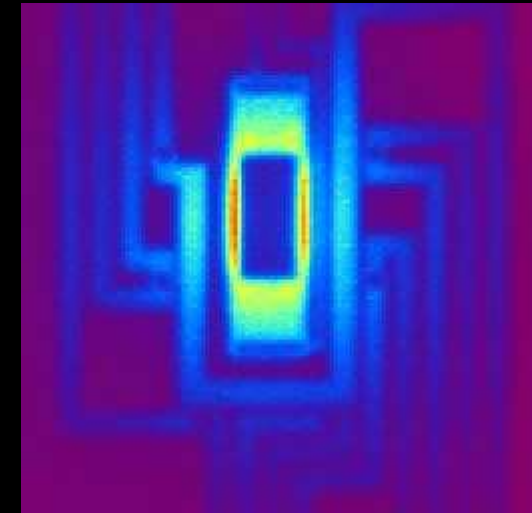
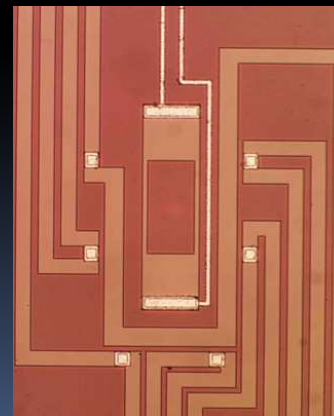
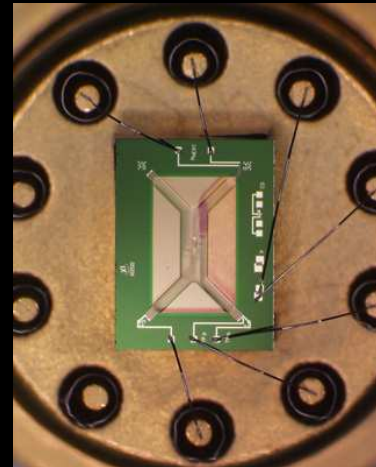
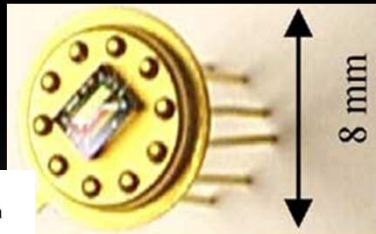
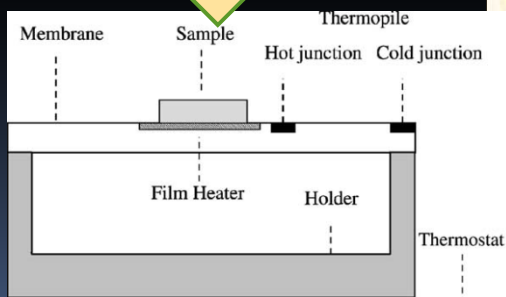


what says "each thermodynamics" ?

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



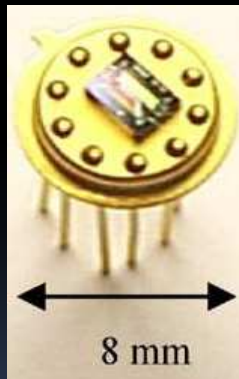
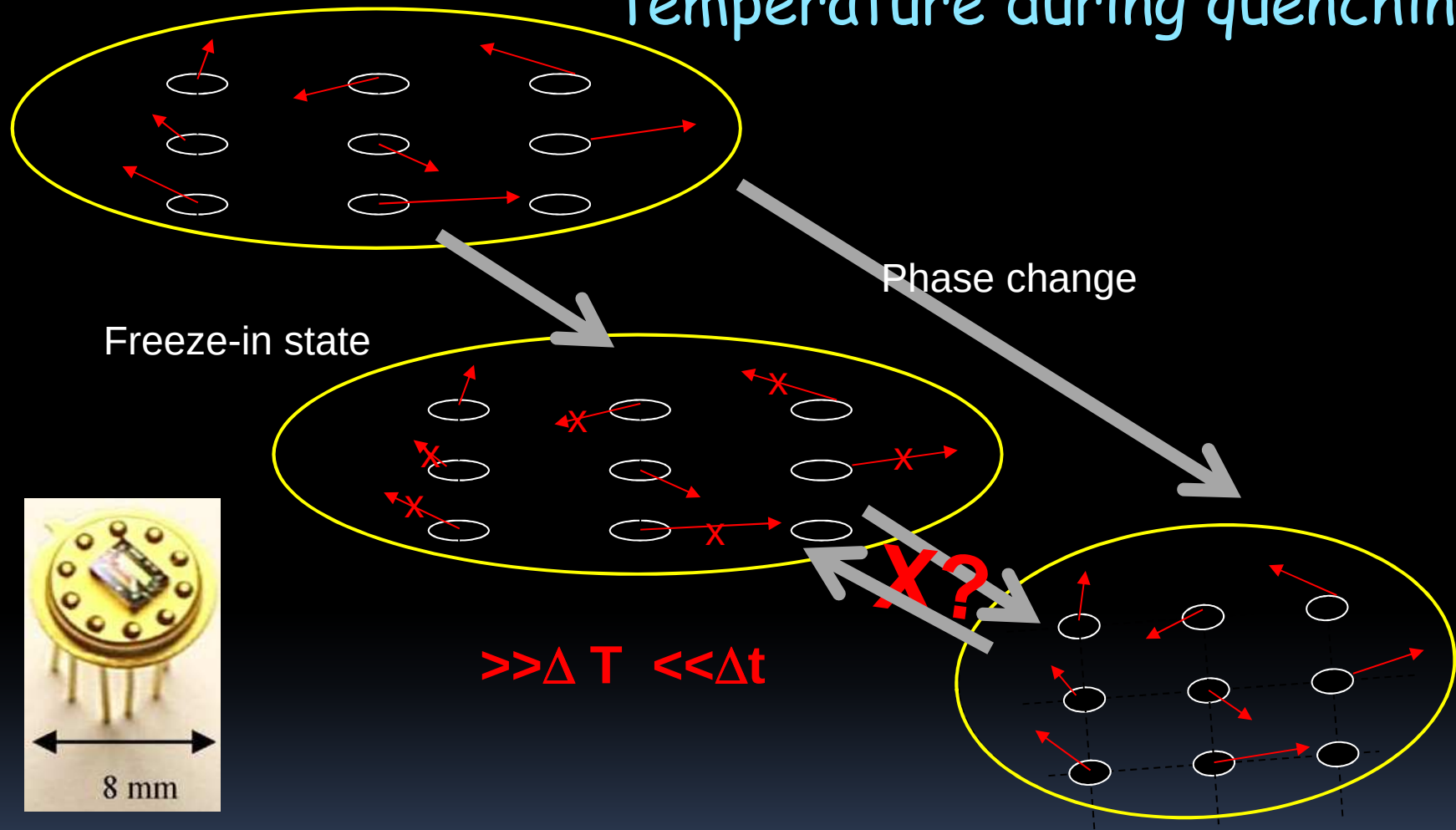
MICROCHIPS



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. (in print)

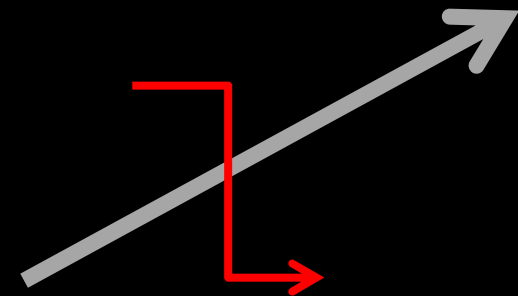
Temperature -tempericity of ultrafast changes (in nano-scale) and its determinability

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

Where is the operate limit of uncertainty principle

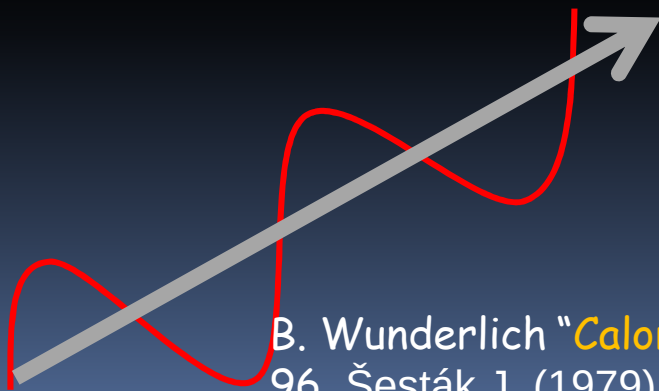
$$\Delta T / \Delta t = ?\Delta?$$

Where is the operate limit of ever recordable temperature changes



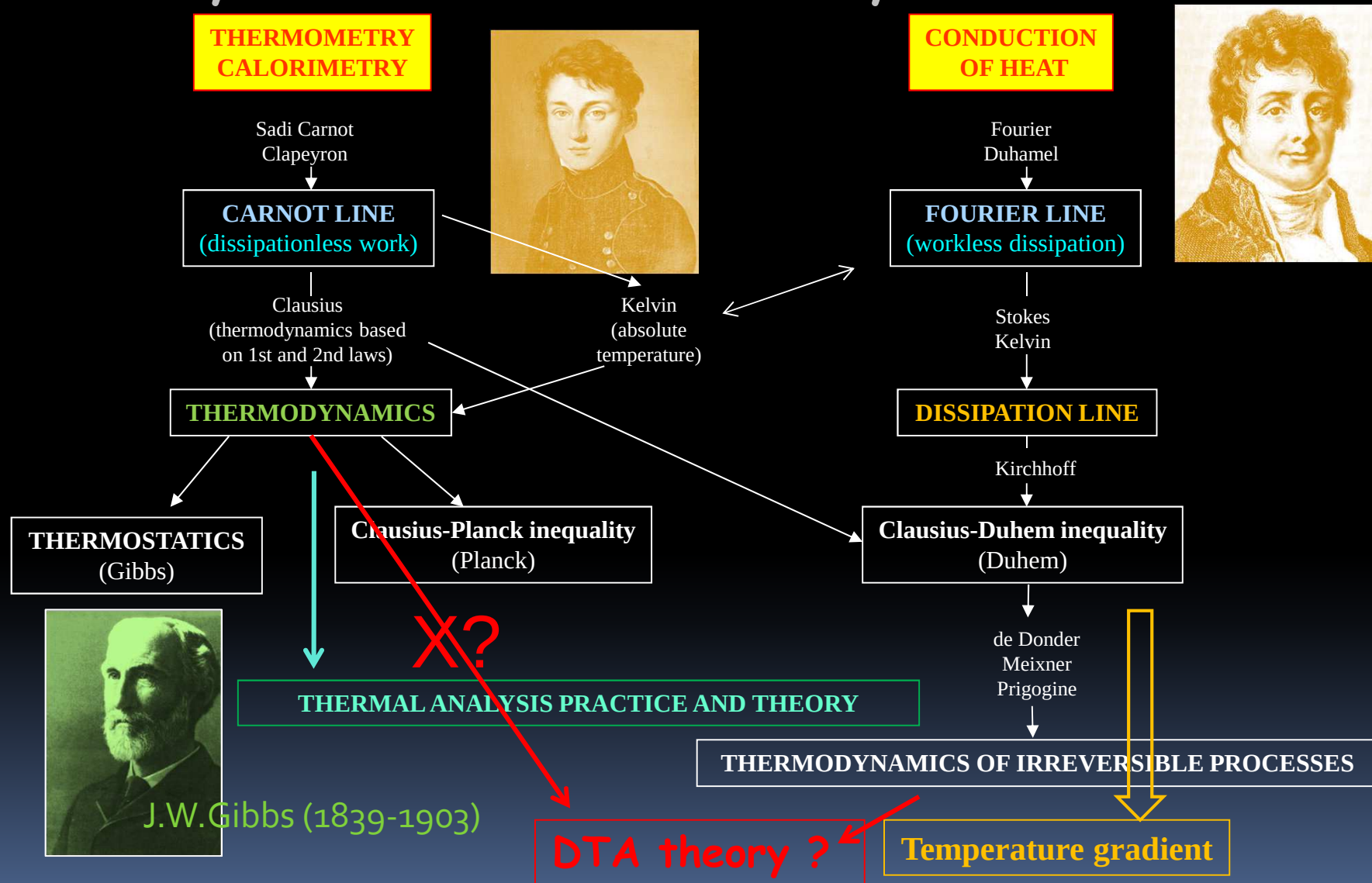
$$\Delta T = ?\Delta?$$

Where is the limit of readable and reproducible temperature gradient



B. Wunderlich "Calorimetry of Nanophases" Int.J. Thermophysics 28 (2007) 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)

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

CONDUCTION OF HEAT

Fourier
Duhamel

FOURIER LINE
(workless dissipation)

Stokes
Kelvin

Clausius-Duhem inequality
THERMODYNAMICS
of irreversible processes

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

Temperature

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

DTA theory ?

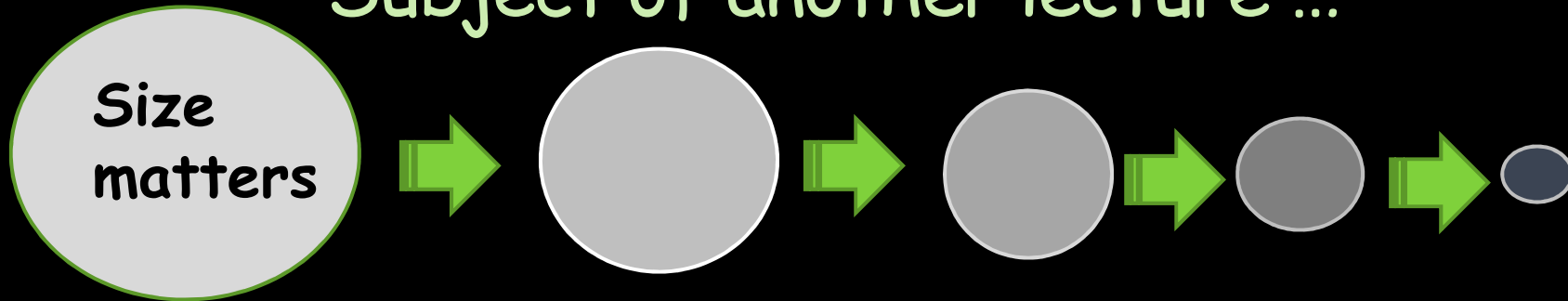
Temperature gradient

Šesták J (2013) Thermal science and analysis: Terms connotation, history, development, and the role of personalities. J Therm Anal Calorim 113:1049–1054

Yet uncertain territory of thermodynamics

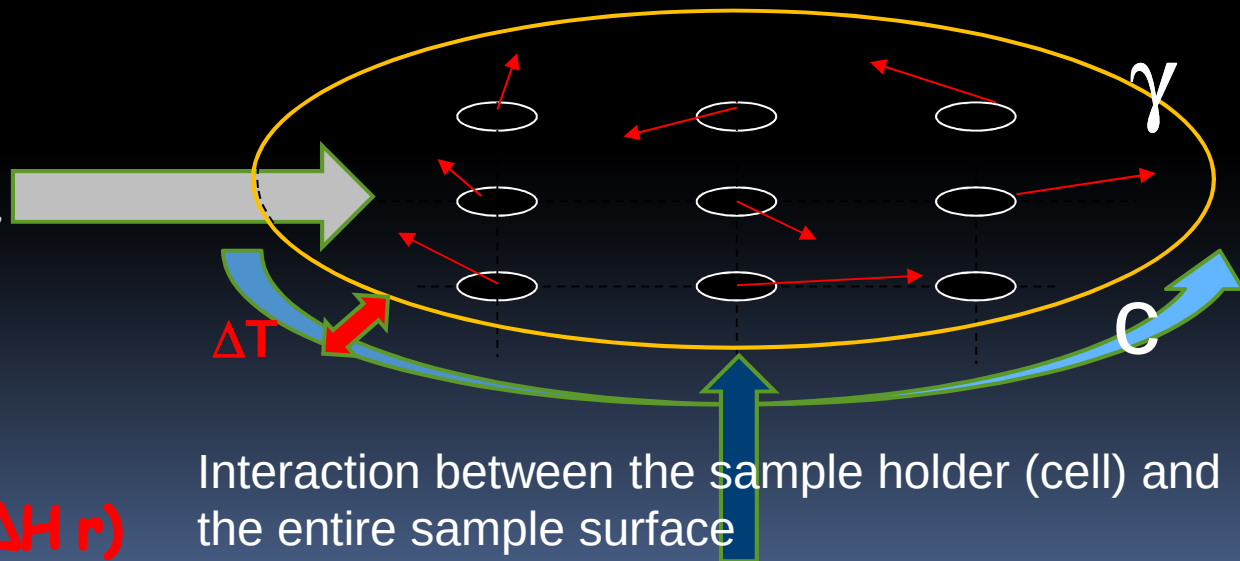
Corrections toward nano-scale progression?

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:

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

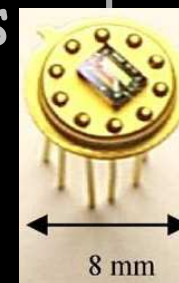
where ∞ portrays a standard state and C and p are empirical constants ranging $\approx 0.15 < C < 0.45$ and $p = 1$ and/or $\frac{1}{2}$

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

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.

...Что пожар не может распространяться на удаленных площадках, то она должна быть контейнером сжатого газа и любые горючие жидкости сразу же помещают в центре пожара.

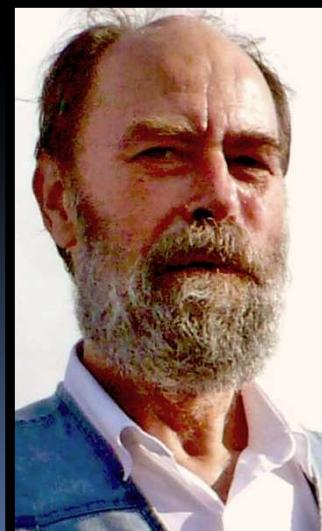
... That the fire could not extend to remote sites, containers of compressed gas and any flammable liquids must be immediately placed in the center of the fire.

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

... Что каждая идея имеет период полураспада, когда она становится глупостью, и наоборот, каждое дерьмо с течением времени становится идея

... That every idea has a half-life when it becomes stupidity, and vice versa, each crap over time becomes an idea



Chybíš nám Pavle !!

