DTA and its historical development, thermodynamics and yet unsettled consequences of the sample heat inertia and temperature gradients

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**SEARCH FOR INFORMATION**

*Information transducer*

**Type of analysis**

- X-RAYS
- HEAT
- QUESTION

**Data treatment**

- DIFFRACT.
- PATTERN
- TA
- CURVE
- PSYCHO
- TEST

**Instrumental interface**

**Evaluation procedure**

- Optical ~ 600 nm (set-up of crystals)
  - Zacharias Janssen (1580-1658);
  - Galileo Galilei (1564-1742)

- X-ray ~ 0.5 nm (ordering of atoms)
  - Max von Laue (1879-1960)
  - William Lawrence Bragg (1890-1971)

- Thermal
  - thermodynamic principles
  - THERMAL STATE

- Psycho
  - psychiatric rules
  - STATE OF MIND

- Sigmund Freud (1856-1939)

**Nondestructive**

**Destructive**

Gustav H.J. Tammann (1861-1938)
Nikolaj S. Kurnakov (1860-1941)
-\Delta W

Mechano-measurements
~ 10 \mu m (>10^{-2} mm)
(external heat response)

Optical-measurements
~ 600 nm (5 \times 10^{-4} mm)

Recently novel
Electron microscopy
~ 10 nm (10^{-5} mm)

X-ray-measurements
~ 0.5 nm (10^{-7} mm)

internal (molecular) heat response)
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

Does it exist?

Similarity ↑

Dissimilarity ?

Physicochemical methods

Spectroscopic methods

Heat transfer methods

DTA
Impact of heat upon the sample inner make up

Changes in vibrational and positional structure

Thermal analysis determination of heat changes

and its sink

upon the sample inner make up

Changes in vibrational and positional structure
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.

Any matter transport desires definite time lag.

Fluid-like transfer

Heat sink within the sample thermal capacity
Isothermal and non-isothermal measurements: naturally involves thermal setups-gradients

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

Mutual comparison of the sensitivity of measurements

Can we recognize its consequences?!
Crystal order by X-ray diffraction screening

X-ray: nondestructive interaction

Acting through crystal interface

DTA: destructive shift of ordered species or modes

Thermal reordering by thermal analysis

ANALOGY

CURVES

apparent
What is the difference?!

Nondestructive immediate response    Heat transfer destructive distortion

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
What reveals a DTA peak

Base line - steady thermal state of structural makeup

Peak, singularity: due thermal state response upon the gradually integrated structural changes

Affected by the sample set up and trial/experimental arrangements
Thermodynamic approach through the detailed analysis of family tree of thermodynamic subdivisions:

**THERMOMETRY**
- Sadi Carnot
- Clapeyron

**CALORIMETRY**
- Carnot Line (dissipationless work)
- Clausius (thermodynamics based on 1st and 2nd laws)

**CONDUCTION OF HEAT**
- Fourier Duhamel
- Kelvin (workless dissipation)
- Stokes Kelvin

**CARNOT LINE**
- Kelvin (absolute temperature)

**FOURIER LINE**
- Kelvin

**THERMODYNAMICS**
- Clausius-Planck inequality (Planck)
- Clausius-Duhem inequality (Duhem)

**THERMOSTATICS**
- (Gibbs)

**DISSIPATION LINE**
- Kirchhoff

**THERMAL ANALYSIS PRACTICE AND THEORY**

**J.W. Gibbs (1839-1903)**

**DTA theory?**

**Temperature gradient**

- de Donder
- Meixner
- Prigogine

**THERMODYNAMICS OF IRREVERSIBLE PROCESSES**
Theoretical basis of thermal analysis

**Thermal Methods of Analysis**
Second Edition
Wesley Wm. Wendlandt

**Thermal Analysis**
Benedict Wunderlich
The University of Tennessee at Knoxville, Knoxville, Tennessee and
Oak Ridge National Laboratory, Oak Ridge, Tennessee

**Generalised Approach to Thermal Analysis**

**Science of Heat and Thermophysical Study**

**KLAUS HEIDE**
**Dynamische thermische Analysenmethoden**

Historical approaches toward theoretical basis of DTA


So far including theory of thermal inertia effects


Macroscopic sample arrangement
Response of a measuring device
Analysis of the responded curves (peaks)
Application of theoretical basis for

Heat transfer + Thermodynamics

Heat pulse introduction into the sample

Surprising response: can we recognize its true meaning?!
Original and corrected (rectified) DTA curve

\[ \Delta t H \text{ heat and } \xi \text{ degree of transition, } t \text{ time.} \]

\[ \Delta T_{DTA} = \left\{ \Delta K(T_W - T_R) - (C_P^S - C_P^R) \Phi - C_P^S (d\Delta T/dt) + \Delta t H. d\xi/dt \right\}/K_{DTA} \]
\[ \Delta T K_{DTA} = \]
\[ + \Delta H_S \xi' \]
\[ - (C_{pS} - C_{pR}) \phi \]
\[ - \Delta C_{pS} (\phi + \Delta T/\text{dt}) \]
\[ - C_{pS} \Delta T/\text{dt} \]
\[ + \Delta K(T) \]

measured quantity
enthalpy evolved
heat capacity change
inertia
transient
experimental constant

1 - as-received DTA
2 - corrected DTA peak
3 - real (s-shaped) background
4 - approximated DTA peak baseline
5 - recorded i.e. actual DTA trace
6 - baseline shift due to the unequal heat capacities
7 - difference in the heat transfer coefficients between the sample and reference
Previous: M.J. Vold (125 citations) provided her equation 8 in above reference as

\[
\frac{\Delta H}{C_S} \frac{da}{dt} = - \left( \frac{d\Delta T}{dt} \right) - A(\Delta T - \Delta_0 T)
\]

where \( \Delta_0 T \) means a level of signal background, \( C_S \) is heat capacity of sample and \( A \approx K/C_S \). The equation (which is nearly equivalent to our equation) was obtained via a complicated derivation which is starting with a typing error “\( dH/dt = (dH/dt)(dT/dt) \)” what could be a reason why the equation was not very credible for a majority of thermoanalysts. The results of Vold was detailed by I. Proks [42] who combined them with results of others authors to derive the dependences of peak area and of position and height of extreme deviation (on the DTA curve) upon heating rate.

In 1957 the mentioned inertia term was used by H.J. Borchard and F. Daniels (824 citations) who applied DTA to study kinetics of homogeneous reactions in well stirred liquid samples showing:

\[
dH = C_P \Delta T + K \Delta T dt
\]

from which our equation can be obtained by substituting \( dH = \Delta H da \) and then dividing their equation by \( dt \). The correction with respect to heat inertia is included also in their equation expressing the rate constant \( k \) of homogeneous reaction

\[
k = \frac{C_P(d\Delta T/dt) + K\Delta T}{(K(A-a) - C_P\Delta T)}
\]

(where \( A \) is total area of peak and \( a \) is a part of this area for time \( t \)).
Effect of heat inertia on kinetic evaluations

Evaluation of kinetics and mechanism by SQUEST

Phase transition of BaCO₃ at 810°C

<table>
<thead>
<tr>
<th>ΔH</th>
<th>E [cal]</th>
<th>mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>613</td>
<td>118</td>
<td>A3</td>
</tr>
<tr>
<td>617</td>
<td>52</td>
<td>A3</td>
</tr>
</tbody>
</table>

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

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 $\alpha_H$ is greater than that of the reference material $\alpha_R$ ($\alpha_H > \alpha_R$).

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
Real form of a DTA peak at the cylindrical location when integrating inherent temperature gradients

\[ \Delta T = \psi \Delta T \]

\[ \Delta T_S = T_{Sf} - T_{SE} \] due to average gradients, \( T_{Sf} = \frac{2}{r_E^2} \int_0^{r_E} T(r) r dr \)
Kinetic models of a phase transition

Continual model:

\[ \alpha = 0 \]

Discontinual model:

\[ \alpha = 1 \] (initial)

\[ \alpha = 0 \] (final)
Variants of kinetic models of a phase transition

continual model:

Discontinual model:
Profile of temperature gradient in the sample at the degree of transition $\xi = 0.7$ assuming a discontinued model.
Continual model of a phase transition - computer calculated
Total (global) degree of transition: $\alpha_G$

Thermal inertia from temperature changes $T_{SE}$ on the sample surface.

Thermal inertia from temperature changes $T_{SE}$ derived by integration over the thermal field inside the sample.

Approaching the reality - who cares?
Not knowing well the thermal nature in a classically arranged sample we are seeking for yet novel methods applying more and more complex thermal regimes.

Amplitude of the radiation intensity $I(x, y)$ measured at ac heating (2 V, 1 Hz). Dashed line A indicates the direction at $y1 = -24 \mu m$ along which the dependence $I(x, y1)$ was measured.
Temperature modulation

Computer calculations ⇒

- Real response

- Inserted modulation

- $T(t)$

- $r$ (time)
Ultra-fast processes - what is temperature contrivance of thermodynamics

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

what says “each thermodynamics”?
Special case of a change: temperature during quenching

Freeze-in state

Phase change

$\Delta T \ll \Delta t$

Temperature of ultrafast changes in nano-scale and its determinability

\[ \Delta q \Delta T = \Delta \Delta? \]
Where is the operate limit of uncertainty principle

\[ \Delta T/\Delta t = \Delta \Delta? \]
Where is the operate limit of ever recordable temperature changes

\[ \Delta T = \Delta \Delta? \]
Where is the limit of readable and reproducible temperature gradient

Yet uncertain territory of thermodynamics

Corrections toward nano-scale?

At macroscopic scales:

the Laws are perfectly valid  but

what happens at nano-scales (curved interfaces)?

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

Interaction between the sample holder (cell) and the entire sample surface (competition between the bulk ~ \( r^3 \) and surface ~ \( r^2 \) )
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 $T_\infty$) 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:

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

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

Micro/nano-analysis of materials

Wunderlich, B.: Calorimetry of nanophases of macromolecules. Int. J. Thermophys. 2007; 28, 958-967

Höhne GWH. Calorimetry on small systems - a thermodynamic contribution. Thermochim Acta 2003; 403: 25-36


Veritas VI, Saamani K. Size and mechanics effects in surface-induced melting of nanoparticles Nature Communications 2011; Volume: 2: 284-296,
Yet further problems at the nano-scale physics:

Heat transfer on submicro- and nano-scales differs from that at macro scale due to:

Finite size of gas gaps (molecules, species) ; so called ballistic effect

Finite thickness of solid domains (photons, electrons) ⇒ ballistic effect

In narrow gaps heat flux limited by velocity and concentration of molecules

Destructing effects on phase interfaces (including destructive interference - phase interface does not have volume))

Thermal photon tunneling (evanescent waves)
Stationary versus dynamic heat capacity

Careful when going behind the ordinary limits!

1. At small space scales we must be very careful when applying the first and second law of thermodynamics. If we measure heat, for example, we should justify what we really do (modulated techniques and/or small samples).

2. The second law has a statistical character at small scales! (needs a special application)

3. At fast processes seems the situation becomes alike that of quantum mechanics, i.e., the coincident measure of accurate temperature and/or heat flow emerge awkward.

4. There are other open questions (gradients, interfaces, crystal size, contacts, fractal behavior, etc.) due to experimental set ups (interfacial contacts ⇒ gradients).

\[ \Delta T \Delta q \Rightarrow \text{limit } \Delta? \Delta? \]

Uncertainty principle in quantum mechanics

\[ \Delta p \Delta x = h \]
Any experiment **always** provides certain data on temperature and other measured variables!

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)
Various scientific views and practices compete each other: who is right in DTA?

Traditional evaluation should be changed but it would bring to many inconvenience in existing (software) practice (evaluations)

Traditional evaluation is necessary to be adjusted because it does not comply to modern theories of thermal gradients

It's not politics; is really the best the only one which is the easiest, loudest or most applauded one?
I appreciate that you kindly waited until the end of my long lecture
thank you