



Šesták's proposal of term “tempericity” for non-equilibrium temperature and modified Tykodi's thermal science classification with regard to methods of thermal analysis

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Abstract The equilibrium (thermodynamic) temperature of a body is defined by zeroth law of thermodynamics as a quantity obtained by thermometer as a result of thermal equilibrium between the body and the thermometer. However, the term temperature is also used for description of any instantaneous thermal state during processes where no thermal equilibrium is reached. The proposal of Tykodi to divide thermal science into three branches has been modified to express the dependence of temperature on time and position inside a system. The three branches have been called thermostatics (equilibrium thermodynamics), thermostatics (thermodynamics of steady = stationary states) and thermokinetics (thermal science dealing with unsteady—non-stationary states). Equilibrium temperature is used only at thermostatics. For other branches of thermal science where the Newton cooling law and/or any of both Fourier laws are applied, no equilibrium temperature with respect to zeroth law is expected. Thermal analysis studying unsteady states (temperature is a function of time t as well as of space coordinates x) should be subject of thermokinetics, and the appropriate kinetic models should include the local temperature changes evoked by self-cooling or self-heating due to process running inside sample.

Keywords Temperature · Thermal equilibrium · Heat inertia · Thermostatics · Thermosteadics · Thermokinetics · Thermal analysis · Non-isothermal kinetics · Local thermokinetic models

Pavel Holba: Deceased.

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There will come a time when our descendants will be amazed that we did not know things that are so plain to them (Veniet tempus, quo posteri nostri tam aperta nos nescisse mirentur). Seneca Younger.

Introduction

Šesták in his essay [1] submitted to JTAC pointed out the difference between the thermodynamic (equilibrium) temperature as *physical quantity* complying with the zeroth law of thermodynamics and a reading displayed by thermometric device under non-equilibrium conditions (e.g., at fast microchip TA methods [2]) as *operational quantity* called “tempericity”.

Šesták's inspiring paper provoked me to specify the problem of temperature in thermal analysis in a somewhat wider context and to propose classification for thermal states according to different roles of temperature in relations applied to thermal phenomena. The classification is derived from the proposal by Tykodi [3, 4] (from 1968) to divide thermal science (“thermotics”) into three branches as it is mentioned in Šesták's paper [1].

Thermodynamic temperature was probably first defined by Maxwell in his Theory of Heat (1871) [5] by the words: “The *temperature* of a body is its thermal state considered with reference to its power of communicating heat to other bodies that body which gives out heat is said to have a higher temperature than that which receives heat from it” and thermal equilibrium as “If bodies are placed in thermal communication and none of them loses heat or gains heat, two bodies are said to have equal temperatures or the same temperature. The two bodies are then said to be in *thermal equilibrium*.” This definition later called as *zeroth law of thermodynamics* is often presented in a brief form: “If system A is in thermal equilibrium with system C and

system B is also in thermal equilibrium with system C, system A and system B are in thermal equilibrium with each other”.

Non-equilibrium temperature and apparent temperature as a measure of thermal comfort for human body

It is known that non-equilibrium temperature is displayed on thermometer when the thermometer is exposed to *sunshine*. In such a case, three bodies are in thermal contact: the thermometer (temperature T_t), air environment (T_e) and Sun (T_s) with heat fluxes ($J \equiv dq/dt$ in W) between Sun and thermometer (J_{St}) and between air environment and thermometer (J_{et}) when air environment and Sun can be considered as inexhaustible thermal reservoirs not changing their temperatures. In such a case, no thermal equilibrium but only stationary state can be reached when number displayed on thermometer (in a dry windless weather) corresponding to the stationary states is given by a simplified relation

$$T_t = [A_{et}(T_e - T_t) + A_{St}(T_s^4 - T_t^4)]/C_t \quad (1)$$

where A_{et} and A_{St} represent heat transfer coefficients for fluxes J_{et} and J_{St} , respectively, and C_t is an effective heat capacity of thermometer.

Similarly, the non-equilibrium temperature can be displayed by thermometer covered by *film of water* and exposed to *air flow* (wind) where evaporation into or condensation from the humid atmosphere can be a heat source or heat sink affecting the reading of temperature. If the rate of water evaporation ($E_w \equiv dm_w/dt$ in g/s, ΔH_{ew} is enthalpy of water evaporation in J/g) or condensation (as negative evaporation) is proportional to velocity of wind v_e , then reading of wet thermometer is determined approximately by

$$T_t = [A_{et}(T_e - T_t) - E_w(v_e)DH_{ew}]/C_t \quad (2)$$

At a sufficient velocity of air flow, the temperature of wet thermometer reaches the *dew point temperature* and remains the same if the velocity is increased. This dew point represents the temperature of equilibrium between water vapor in air and liquid water but not the equilibrium temperature of surrounding air.

Both examples show the non-equilibrium reading of thermometer due to additional source (or sink) of heat in a system. However, these non-equilibrium temperature readings correspond to sensation of thermal state by human body covered by a thin film of sweat and can serve as a measure of thermal comfort for the body.

Non-equilibrium temperature due to heat inertia

The more frequent displaying of non-equilibrium temperature is due to time delay—slow adaption of any object in system under study to the required temperature of environment. This phenomenon called also as *heat inertia* effect [6–18] is usually omitted at processing of outputs of thermoanalytical experiments. The phenomenon is usually manifested as a delay of the sample and/or reference temperature with respect to a temperature demanded by heating program.

The simplest correction of heat inertia effect at DTA and spontaneous heat flux DSC consists in use of the following adequate equations:

$$\begin{aligned} \text{a) for DTA : } \Delta T &= R_{\text{eff}}(-C_s d\Delta T/dt - \Delta H d\alpha/dt) \\ &\Rightarrow d\alpha/dt \neq -\Delta T/A_{\text{DTA}} \end{aligned} \quad (3)$$

where $\Delta T (= T_s - T_r)$ is the difference between the sample temperature and the reference temperature, ($d\Delta T/dt$ is then the time derivative of this difference), $R_{\text{eff}}(T)$ is the effective thermal resistance of heat flux, C_s is the heat capacity of the sample, ΔH is the change in enthalpy corresponding to the process inside sample, α is the degree of conversion of this process ($d\alpha/dt$ is then the rate of the process) and $A_{\text{DTA}} = \int \Delta T dt \equiv R_{\text{eff}} \Delta H$ is the area of DTA peak (in Ks—Kelvinseconds)

$$\begin{aligned} \text{b) for spontaneous heat flux DSC : } J_q \\ = -C_s dJ_q/dt - \Delta H \cdot d\alpha/dt \Rightarrow d\alpha/dt \neq -J_q/A_{\text{DSC}} \end{aligned} \quad (4)$$

where $\Delta T (= T_s - T_r)$ is the difference between the sample temperature and the reference temperature transformed into heat flux (in W) between the sample and reference (using $R_{\text{eff}}(T)$ which is determined by calibration at several temperatures; dJ_q/dt is then the time derivative of this heat flux) and $A_{\text{DSC}} = \int J_q dt \equiv \Delta H$ is the area of DSC peak (in W).

During any process taking place inside the sample, temperature of the sample T_s is not the equilibrium temperature. It differs from linearly increasing or decreasing reference temperature T_r or other temperature T_{env} representing thermal state of the sample surroundings (e.g., T_{block} at DSC) as a consequence of self-cooling or self-heating caused by the running process inside the sample.

The mentioned corrections (3) and (4) follow from Newton's cooling law [19] which are in accordance with Tian [20], Vold [21] and Borchardt and Daniels [22]; however, the last authors have meant that the heat inertia term in DTA equation is negligible. This neglect is included by, e.g., Kissinger [23] and Piloyan et al. [24], but it is respected (besides work of our research group [6–18])

only by Factor and Hanks [25] and Chen and Kirsh [26]) and used by Pérez et al. [27]. It should be noted that the corrections of time-delay effect based on the idea of thermal circuits are also used (see, e.g., [28]).

The corrections included in Eqs. (3) and (4) are not fully sufficient because also in the absence of self-heating or self-cooling (for $\alpha = 0$) the temperature in the sample center T_c differs from the temperature on the sample surface T_{sS} as it was given in [29]. This is a reason why for the compensation DSC (Perkin–Elmer) method the displayed sample temperature is not fully representing the temperature of the sample although no correction on the heat inertia effect is necessary and the condition $\Delta T = 0$ (or $J_q = 0$) is guaranteed by the power compensating device. Temperature of the sample surface does not represent the sample temperature when the temperature field inside the sample is not uniform due to self-cooling or self-heating but also by nonzero heating or cooling rate.

Also in thermogravimetry, where the thermal contact with the sample is not very tight, we do not know the true temperature of sample and the form of TG curve can be affected by the rate of heat transfer between the surroundings and the sample as it was noted by Gray [30].

Modified Tykodi's division of phenomenological thermal science

Tykodi's division of thermal science [3, 4] (Tykodi used Wheller's term "thermotics" [31] for all thermal science) remembered in Šesták's paper [1] is also very inspiring and could explain the difference between the main classes of thermal phenomena.

Tykodi divided various thermal phenomena into (1) thermodynamic equilibrium phenomena as a subject of "thermostatics," (2) steady state phenomena (steady or stationary state is a stable state when local temperatures do not change over time) as a subject of "thermosteadics" and (c) unsteady state phenomena (non-stationary) as a subject of "thermodynamics." However, the term "thermodynamics" is so firmly anchored in science in its contemporary meaning that it will be better to leave this meaning unchanged and call the thermal science dealing with non-stationary phenomena as "thermokinetics." Then, the phenomenological¹ thermal science could be divided into

"thermostatics" where derivatives of temperature T with respect to space coordinates x and to time t are zero: $dT/dx = 0$ and $dT/dt = 0$ (the term thermostatics was already used in sense of equilibrium thermodynamic by van der Waals and Kohnstamm in the title of their book from 1927 [32]), "thermosteadics," where $dT(x)/dt = 0$ but $dT(t)/dx \neq 0$, and "thermokinetics," where derivatives are depending on time ($dT(t, x)/dt \neq 0$) as well as on space coordinates ($dT(t, x)/dx \neq 0$).

In the following paragraphs, a rough characterization of these three regions is proposed together with laws applicable for the corresponding phenomena.

"**Thermostatics**" includes all equilibrium thermodynamics, and it studies equilibrium states which can be distinguished by the fact that the measured temperature T is independent on the local position in system (x) as well as on time t . Then, the equilibrium temperature field $T(x, t)$ inside a given thermodynamic system must be uniform (the same T in any position: **grad** $T = 0$; through all bodies inside the system), and this uniform temperature is time independent ($dT/dt = 0$). At thermostatics, the equilibrium temperature respects the zeroth law of thermodynamics.

For equilibrium states, the thermodynamic laws are valid:

- the zeroth law on temperature T by Maxwell (1871) [3, 4],
- the first law on internal energy U : $dU = dq - dw$ by Clausius (1850) [35]
- the second law on entropy S and its maximum value as a condition of thermodynamic equilibrium state: $S \rightarrow \max$ by Clausius (1865) [36],
- the third law on low-temperature limit of entropy: $\lim_{T \rightarrow 0} S = 0$, by Nernst (Heat Theorem 1906) [37] and verified by Giauque and Mac Dougall (1933) [38–40] and
- all other relations known from textbooks on phenomenological equilibrium chemical and physical thermodynamics Lewis and Randall [38–40], Callen [33, 34], Kvasnica [41], etc.

"**Thermosteadics**" [42] includes studies of all steady states which can be distinguished by the fact that the measured temperature T is independent of time t ($\rightarrow dT(x, t)/dt = 0$). For example, steady states are formed in systems which two non-neighboring (e.g., planar opposite parallel) diathermic walls of system are exposed to reservoirs with different temperatures; however, other walls (rest of surface) of system are adiabatic ones. The temperature $T(x)$ in a point x does not correspond to the zeroth law of thermodynamics when the constant temperature is reached not by thermal equilibrium but by the balance between heat flux coming into the point x from one direction and the heat flux departing from other point in opposite direction.

¹ Statistical thermodynamics—see Gibbs 1902 [32]—or "thermostatistics" (as proposed by Callen in title of his book from 1985 [33, 34]) can be considered as non-phenomenological division of thermal science.

For steady states, the following laws are valid:

- Fourier's first law for heat flux (in one-dimensional case, e.g.):

$$J_q \equiv dq/dt = \lambda AdT/dx \quad (5)$$

where J_q , λ and A stand for the heat flux, thermal conductivity and cross-sectional area of thermal conductor, respectively [43]

- Onsager rate of entropy production and reciprocal relations from 1931 (see [44, 45])
- Entropy production extremum: $dS/dt = 0$, minimum by Prigogine (1945) [46], extremum by Ziman [47] and maximum by Jaynes [48, 49]

“**Thermokinetics**” derived from Greek word κίνησις = motion, movement) deals with states which are not equilibrium nor steady states; for the unsteady states, the temperature field $T(x)$ in the sample (local temperatures) changes with time. All the states existing during heating or cooling are unsteady states so that any region of usual thermoanalytical experiments is based on unsteady states and, as a consequence, on measuring the non-equilibrium temperatures.

For unsteady states, the following laws are valid:

- Newton's cooling law

$$C_b(T_b - T_{env}) = -\lambda dT/dt \quad (6)$$

discovered in 1701 [19] where temperature of a body $T_b > T_{env}$ (temperature of environment as an inexhaustible thermal reservoir), C_b stands for the heat capacity of body and λ is the heat conductance. If $T_{env} = \text{const}$, then $dT = d(T_b - T_{env})$, and we have

$$dt = -(A/C_b)d \ln(T_b - T_{env}) \quad (7)$$

and after integration we obtain

$$t - t_0 = -(A/C_b) \ln((T_b(t) - T_{env}) / (T_b(t_0) - T_{env})), \quad (8)$$

which can be transformed into

$$(T_b(t) - T_{env}) = (T_b(t_0) - T_{env}) \exp(-(t - t_0)/t), \quad (9)$$

where $\tau \equiv C_b/A$ is called the time constant of cooling (the equations are valid also for heating $T_b < T_{env}$).

- Fourier's second law for temperature change (heat equation derived from [43]):

$$\begin{aligned} dT/dt &= (\lambda/C)(\partial^2 T/\partial x^2 + \partial^2 T/\partial y^2 + \partial^2 T/\partial z^2) \\ &\equiv (\lambda/C) \mathbf{div grad} T \equiv (\lambda/C) \nabla^2 T \end{aligned} \quad (10)$$

where λ and C are the heat conductivity and heat capacity, respectively ($a \equiv \lambda/C$ is called the thermal diffusivity).

It seems that three branches of thermal science correspond to disciplines encompassing different formalisms. According to Lebon et al. [50], three thermodynamic formalisms can be defined as:

- Equilibrium thermodynamics (ET), e.g., in conception of Callen [33, 34], studying macroscopic properties of systems that are in mechanical, thermal, electric, magnetic and chemical equilibrium.
- Non-equilibrium thermodynamics (NET) or thermodynamics of irreversible processes according to de Groot and Mazur [51], who used formalism based on hypothetical “principle the local equilibrium.”
- Extended non-equilibrium thermodynamics (ENET) according to Jou and Lebon [52], studying systems where the local equilibrium hypothesis is not valid using thermodynamic mixed formulations.

Thermal analysis as a part of “thermokinetics”

As stated above, in thermoanalytical experiments we deal with neither equilibrium states nor steady states but only with non-steady states where the thermal equilibrium cannot be reached. By the approximation to zero heating rate, we are able to estimate equilibrium temperatures of transitions (as well as enthalpy, mass or length integral changes); however, the higher the heating/cooling rate, the higher the difference between the temperature of the sample center and the sample surface. This difference can be estimated only for a thermally inert sample (without any transition or reaction in a given temperature interval) assuming thermal diffusivity α to be almost temperature independent.

Using heat transfer equation, we are able to calculate the temperature field (radial profile) for linear heating rate ($\beta = dT/dt$) in a thermally inert (without transitions or reactions indicated by the change in temperature) sample [29] as “stabilized temperature profile” (dependence of temperature on coordinates)—e.g., for the coordinate r (radial distance from the rotation axis in cylindrical sample with infinite height) as

$$T(r, t) = T(t_0) + \beta[(t - t_0) - (R^2 - r^2)/4a] \quad (11)$$

assuming $T(R, t) = T(t_0) + \beta(t - t_0)$, where r is the distance of position to axis ($r = 0$) of cylinder, R is the external radius of cylinder, T_0 is the initial temperature at time t_0 and $a = \lambda/(\rho C)$ is the thermal diffusivity. The instantaneous average (weighted) temperature $T_\phi(t)$ through all volume of the sample is then given as

$$T_\phi = T(R, t) - \beta R^2/8a \quad (12)$$

We are able to indicate only the temperature near the sample surface $T_{ss} = T(R, t)$, and it follows from the latter equation that the difference between the surface and the average temperature is proportional to the product βR^2 .

It seems the fast scanning calorimetry [2] (and its variants) handles with temperature by a similar way as classical methods of thermal analysis. Moreover, the competent recommendation for temperature calibration [53] has been published, and an analysis of heat inertia and temperature distribution has been performed [54, 55].

Great mistakes of classical thermal analysis are accompanied with the attempts to discover mechanisms of "heterogeneous kinetics" from TA output. All the attempts are based on separability of function $F(\alpha, T)$ in "general kinetic equation"

$$d\alpha/dt = F(\alpha, T) = f(\alpha)k(T) \tag{13}$$

where temperature T is identified with a temperature of linear heating or cooling program $T_{pr} \approx T_{env} \approx T_r$. However, the temperature in the general kinetic equation is not the programmed temperature T_{pr} nor temperature of sample environment T_{env} (or reference sample T_r) but the temperature of sample T_s which is (during the investigated process) decreased by self-cooling or increased by self-heating due to the enthalpy change accompanying the process. The difference between the temperature of sample T_s and the programmed linearly time-dependent temperature T_{pr} is roughly proportional to the rate of the process $T_s \approx T_{pr} + \Delta T$ where

$$\Delta T = R_{eff}(-C_s d\Delta T/dt - \Delta H d\alpha/dt) \tag{14}$$

so that

$$T_s = T_{pr} - R_{eff}(-C_s(dT_s/dt - \beta) - \Delta H d\alpha/dt) \tag{15}$$

(where $\beta = dT_{pr}/dt$). The general kinetic equation should be written as

$$\begin{aligned} d\alpha/dt &= F(\alpha, T_s) \\ &= F(\alpha, T_{pr} + C_s(\beta - dT_s/dt) - R_{eff}\Delta H(d\alpha/dt)) \end{aligned} \tag{16}$$

and if $(d\alpha/dt)$ is a function of α , then T_s is also a function of α and no separability of $F(\alpha, T_s) \neq f(\alpha)k(T_s)$ into product of $f(\alpha)$ and $k(T_s)$ can be assumed.

Even in the case that the temperature of sample T_s is correctly included into the kinetic equation, the other problem is not solved: We know only temperature of external surface of sample T_{ss} which does not represent unambiguously the actual temperature field $T(r)$ (dependence of temperature on local coordinate r in the case of

infinite cylinder) inside the sample. This temperature field is during the process influenced by self-cooling or self-heating so that the adequate kinetic model should propose two dependences: a) for development of local temperatures $T(r, t)$ and b) for development of local degree of conversion/transition $\alpha(r, t)$ to formulate an adequate kinetic equations

$$d\alpha(r)/dt = F(r, \alpha, T) \tag{17}$$

In [29], we tried to construct a local continuous kinetic model for enantiotropic phase transition using the simplest possible kinetic relation of local ($r =$ radial distance of the local point from axis of sample in form of infinite cylinder) transition rate

$$d\alpha(r)/dt = k(T)(T(r) - T_{eq})(1 - \alpha) \tag{18}$$

guaranteeing zero rate of enantiotropic transition at heating before the transition equilibrium temperature T_{eq} is reached and in the moment when transition is over. Such a model respects the limiting role of thermodynamic equilibrium (equilibrium background [56, 57]) for the rate of enantiotropic transition processes which is also neglected in usual methods of kinetic evaluation; however, the model neglects any delay of transition onset due to a nonzero activation energy. The mentioned model can include the influence of hydrostatic pressure P if we consider T_{eq} as function of P (i.e., $T_{eq} = T_{eq}(P)$) when the dependence of T_{eq} on P is given by the Clausius–Clapeyron equation

$$\begin{aligned} d \ln T_{eq}/dP &= \Delta V/\Delta H \quad \text{or} \\ \ln(T_{eq}(P_o)/T_{eq}(P)) &= (P - P_o)\Delta V/\Delta H \end{aligned} \tag{19}$$

The simple kinetic model for enantiotropic solid phase transition expressed by Eq. (18) can be generalized to model of any solid phase transition by usual substituting $k(T)$ by Arrhenius equation (with pre-exponential factor Z and activation energy E)

$$k(T(r)) = Z \exp(-E/RT(r)) \tag{20}$$

or by other temperature dependence (see [58])

We were able to derive continuous model in [29] for phase transition under condition that nucleation of new phase in a given point r is random and not influenced by existence of the new phase in the neighbourhood of this point. However, a discontinuous model, where the transition interface is shifting from outer shells to the center of cylinder, is more probable. Temperature distribution in such a case is divided by this interface into outer part and central part according to old idea of Smyth [59].

Conclusions

1. Data displaying on thermometer as temperatures under conditions of non-isothermal heating or cooling are not equilibrium temperatures corresponding to the zeroth law of thermodynamics.
2. Apparent temperature of solid sample T_s is not equal to programmed temperature T_{pr} adjusted by heating or cooling regime since the sample shows some thermal inertia and its temperature is influenced by self-cooling (or self-heating) due to the process running inside the sample.
3. The information on temperature of solid sample T_s at a given time t does not represent the instantaneous thermal state (thermoscopic state—see [60]) of the sample nor average (weighted) temperature T_ϕ of the sample but only temperature of the sample surface T_{sS} (or of sample holder T_{sH}).
4. Thermal state of the sample can be represented by instantaneous temperature field inside sample, which can be expressed for a point with coordinate r (radial distance from vertical rotation axis) of infinite cylindrical sample as $T(r)$. Such a temperature field depends on dimensions of the sample, on heating/cooling rate and is mutually connected with the space distribution of transition degree $\alpha(r)$.
5. Knowledge of the thermal state of solid sample is necessary for construction of new generation of kinetic models (called, e.g., thermokinetic models) expressing local kinetic equations in a form:

$$d\alpha(r)/dt = F(\alpha(r), T(r)) \quad (21)$$

where the modified Fourier second law (for the sample in a form of infinite cylinder) for the relation between the local transition rate $d\alpha(r)/dt$, local degree of transition $\alpha(r)$ and local temperature $T(r)$ (where λ_s , C_s and ΔH are sample heat conductivity, sample heat capacity and integral enthalpy of transition, respectively)

$$\left[d^2T(r)/dr^2 + (1/r)dT(r)/dr \right] (\lambda_s/C_s) = dT(r)/dt + (\Delta H/C_s) (d\alpha(r)/dt) \quad (22)$$

for any position r .

Such an approach to non-isothermal kinetics requires a new experimental techniques allowing verification of such kinetic models.

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