NON-STEADY-STATE METHODS FOR DETERMINATION OF THERMOPHYSICAL
CHARACTERISTICS OF SOLIDS

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A brief analysis is presented of the process of linearization of the mathematical
thermal conductivity model for determination of thermophysical characteristics by
non-steady-state methods (flash and constant velocity methods).

In practical determinations of thermophysical characteristics of materials and thermal
fluxes, wide use is made of methods based on the principles of the non-steady-state thermal
regime [1, 2]. Kondrat'ev and his school provided a basis for many methods of determining
thermal conductivity λ, specific mass or volume heat c, $c_V = c_\rho$, thermal diffusivity $a = \lambda/c_V$,
heat liberation coefficient α, and specific power of surface or volume heat sources q_s, q_v.
Because of their common attribute (non-steady-state thermal process) such methods are called
"non-steady-state methods" or "methods based on the principles of non-steady-state thermal
regimes" [2]. In [1, 2] the components of the phenomenological thermal conductivity model
enumerated above were developed from so-called "regular regime methods." In the last two
decades dozens of methods based on measurement of non-steady-state temperature fields have
been developed. The "flash method" [3], its modifications, and studies of λ, c, and a with
their aid were the subject of a special study [4]. The analysis of studies published over
the years performed in [4] revealed the intensive development and expansion which "flash"
type methods have experienced. The development of non-steady-state methods commenced when
thermophysicists (then called simply physicists) began the search for coefficients or terms
in phenomenological thermal conductivity equations. Unfortunately, but for completely under-
standable reasons, the majority of non-steady-state methods for determination of λ, c, a, q,
α are based on linear thermal conductivity equations in which those quantities are assumed
constant. At the same time, experimental studies provide λ, c, a values which are to a
greater or lesser degree temperature dependent. Thus, we have one of the paradoxes of thermo-
physics — the mathematical model which serves as a basis for acquisition of phenomenological
thermophysical coefficients is written for constant values of λ, c, a, while the λ, c, a
values obtained by non-steady-state methods are functions of temperature $\lambda(T)$, $c(T)$, $a(T)$. But
the problem is not that they are written as functions of temperature, but that they are ob-
tained from study of linear mathematical models, and should be derived from more complex non-
linear non-steady-state thermal conductivity models (phenomenological equations).

It was shown in [5] that the non-steady-state methods described in [1-3, 6] as well as
others based on a linear model of non-steady-state thermal conductivity can lead to errors in
determining λ, c, a when the real λ, c, a are significantly temperature dependent in the
temperature range existing in experiment. It should be stressed that we are concerned here
with the temperature at which the specimen is maintained, and not the temperatures measured
in the experiment.

Usually in the flash method temperatures are measured on a surface opposite to the heated
surface. A qualitative analysis of the thermal conductivity equation

$$\frac{\partial}{\partial x}\left[\lambda\,(T)\,\frac{\partial T}{\partial x}\right] - c\,(T)\,\rho\,(T)\,\frac{\partial T}{\partial \tau} = 0 \tag{1}$$

will permit an analysis of the error produced by transition from Eq. (1) to a model α = const,
λ = const, c = const, ρ = const, $a = \lambda/c\rho = \lambda/c_V$. Such an analysis was carried out in [7].
The linear model has the form

$$\frac{\partial^2 T_l}{\partial x^2} - \frac{1}{a}\frac{\partial T_l}{\partial \tau} = 0, \tag{2}$$

where the subscript l refers to the temperature in the linear problem. After simple transformations the nonlinear model of Eq. (1) can be written in the form:

$$\frac{\partial^2 T}{\partial x^2} - \frac{1}{a}\frac{\partial T}{\partial \tau} + \frac{1}{\lambda}\frac{\partial \lambda}{\partial T}\left(\frac{\partial T}{\partial x}\right)^2 = 0 \tag{3}$$

or

$$\frac{\partial^2 T}{\partial x^2} - \frac{1}{a}\frac{\partial T}{\partial \tau} + \frac{1}{\lambda}\frac{\partial \lambda}{\partial x}\frac{\partial T}{\partial x} = 0. \tag{4}$$

We will note that in Eqs. (3), (4) $a(T) = \lambda(T)/c(T)$ and $\lambda(T)$, i.e., λ, c_V, a, are functions of temperature.

Even if the value a = const from Eq. (2) is approximately equal to the mean value of $a(T)$ (over some temperature range), it is still true that $T_l \neq T$, since the former depends on the value of the third term in Eqs. (3) or (4), which plays the role of an internal source q_V, which is a function of temperature. Thus, if the experimental values T_e are obtained under the assumption that λ, c, a are functions of T, $f(T)$, there is no way they may be used to obtain a from Eq. (2), since it is assumed that the T_e used in the models corresponding to a physical process, i.e., the model temperature T_{lm} obtained from solutions of Eq. (2), cannot be used to obtain $\lambda(T)$, $c_V(T)$, $a(T)$, which appear in models with Eqs. (3), (4).

The class of inverse (internally converse) thermal conductivity problems (obtaining λ c_V, a, and other characteristics with non-steady-state methods) is one of the class of converse heat-exchange problems [5, 7]. A solution of any converse problem can only be obtained by comparison of T_m and T_e. In reduction (forward) methods T_e is substituted in the reduced solution of the linear problem (2), instead of in Eqs. (3), (4). The solution of the linear problem is unique, so that T_l is not always equal to T. Thus, T_e is not substituted in the problem which physically exists (it is placed in the linear rather than the nonlinear problem). In extremal methods the discrepancy function $\Phi(T_m - T_e)$ is minimized. If in Φ we substitute T_m from an incorrectly formulated direct problem, then the λ, c_V, a obtained will have significant errors. These errors are large in incorrect converse problems due to errors in T_e, but these errors develop because of errors related to the T_m value which has been obtained by a methodologically incorrect technique. These latter errors increase the discrepancy $(T_m - T_e)$, which is equivalent to a growth in experimental error, a growth in ΔT_e.

Below we will present two examples of solutions of converse problems of λ, c, a determination by the flash method [3] and the constant velocity method [6, 8]. In both cases $\lambda(T)$, $c_V(T)$, i.e., $a(T)$, are specified (Fig. 1). Data on λ, c, ρ, and a_T were taken from [9]. Calculations were performed for $c_V = c_\rho$ and a_ρ. Occasionally in the reference literature (see, for example, [9]) calculated a_p values and tabular a_T values (i.e., a values presented in handbook tables) differ. For example, in [7] it was shown that for 08 steel the maximum difference reaches 10%, with a mean difference of 1-1.5%. As a rule, the handbook authors explain such differences as being due to experimental errors in the various studies used in tabulating the handbook. As will become evident below, the differences between a_p and a_T may also be explained by the fact that the calculated a_p values are determined from λ and c_V values determined independently, while a_T is determined by non-steady-state methods which have systemic methodical errors which will be described below. The errors in determining $\lambda(T)$, $c_V(T)$ and $a(T) = \lambda(T)/c_V(T)$ are generated by the error produced by linearizing the mathematical models on which the techniques of [1-4, 6, 8] are based. These and other studies of non-steady-state methods use as a starting point for determining characteristics not nonlinear models (although $\lambda(T)$ and $c_V(T)$ as well as $a(T)$ are obtained explicitly), but linear models of non-steady-state thermal conductivity.

The authors have solved converse problems by the classical "flash" method [3] and the "constant velocity" method [7] with linear models in the calculated expressions and the graphs presented in [3, 8]. As a control, the same converse problems were solved by extremal methods specially developed for solution of converse problems [5].
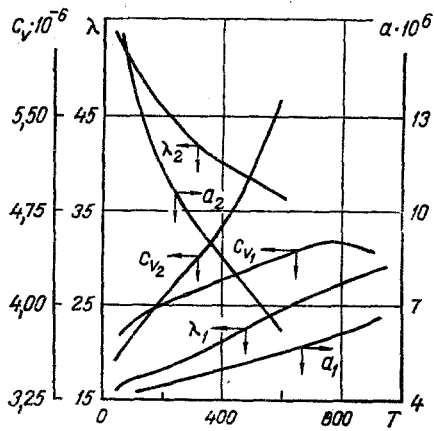
Fig. 1   Fig. 2

Fig. 1. Thermal conductivity coefficient (λ), specific heat at constant volume (c_V), and thermal diffusivity (a) of 1Kh18N9T stainless steel (λ_1, c_{V_1}, a_1) and 20Kh steel (λ_2, c_{V_2}, a_2) versus temperature. c_V, kJ/m³·deg K; λ, W/m·deg K; a, m²/sec; T, °C.
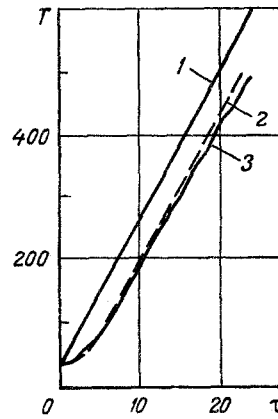
Fig. 2. Change in temperature of surface (1) and middle (2) of plate with time in linear (1, 2) and nonlinear (1, 3) problems. γ, min.

Error in determination of a = const for the flash method comprised 11.5% even when a is referenced to the same effective temperatures as used by the authors of [3]. Errors in a determination by the constant velocity method (see Fig. 2 for temperature curves for the nonlinear problem) comprised from 30 to 85% depending on the heating rate.

We note that the process of referencing a to some effective temperature in [3] is in fact not justifiable and essentially contradicts the model with constant (temperature independent) λ, c_V. In the constant velocity method, because of the original nonlinear model, the $T(\tau)$ curves can never lie in a fashion such that the parallel lines required for finding a are obtained (see curves 2, 3 of Fig. 2).

Values of $\lambda(T)$, $c_V(T)$ (and if necessary $a(T)$) can be obtained by the technique of [5] using the same initial data (experimental model temperatures) with an error significantly less than that of the non-steady-state methods with linear models. Special tests performed in [5] with reference specimens revealed that $\lambda(T)$, $c_V(T)$, $a(T)$ can be obtained for various materials with an uncertainty comparable to the uncertainty in experimental temperature T_e, if extremal methods with regularization by Tikhonov's method [10] are used with a nonlinear model of non-steady-state thermal conductivity.

Thus, the mathematical model used for the non-steady-state thermal conductivity process must correspond to physical reality. If λ, c_V, a are functions of temperature, then one cannot use results from measurement methods based on a linear model to calculate them, without introducing significant error.

In those cases where λ, c_V, and a have been obtained by non-steady-state methods with linear models it is necessary to recheck the data on $\lambda(T)$, $c_V(T)$, $a(T)$ recommended in the reference works. Non-steady-state methods for determining thermophysical characteristics of materials are in fact methods for solving mathematical physics problems, incorrect in the meaning of Adamar, and analysis of results obtained by such methods must be performed with consideration of the errors intrinsic to solution of converse problems.

NOTATION

λ, a, α, c, and c_V = c_ρ, thermal conductivity and diffusivity, heat liberation coefficient, mass and volume heat capacities; $a = \lambda/c_V$; ρ density; T, temperature; q, thermal flux; Φ, discrepancy function; τ, time; x, coordinate. Subscripts: V, volume; m, model; e, experimental; l, linear.

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EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF FORMIATES

AS A FUNCTION OF TEMPERATURE

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Experimental temperature dependences of the coefficient of thermal conductivity of formiates at atmospheric pressure are obtained by the method of monotonic heating.

Data on the temperature dependence of the thermal conductivity of formiates (butyl formiate, propyl formiate, hexyl formiate, and octyl formiate) were obtained by the method of monotonic heating [1]. Chemically clean reagents were investigated. The liquids were first cleaned by distillation in a vacuum, after which their purity was estimated on a Tsvet-4 chromatograph at the Yu. Mamedaliev Institute of Petrochemical Processes of the Academy of Sciences of the Adzerbaidzhan SSR. The analysis showed that the content of the principal product in the reagents was not less than 99.2%.

The experiments were performed at atmospheric pressure at temperatures ranging from room temperature to the normal boiling temperature of the liquid. The molecular weights of the substances studied range from 70 to 186.

When measuring the coefficient of thermal conductivity of the liquids, one of the important problems is the elimination of the influence of convective heat transfer. For this reason, in designing the measuring cell, the construction, geometric dimensions, and temperature conditions were chosen taking this circumstance into account.

In calculating the thermal conductivity, all corrections that are essential for this method were introduced [1]. The maximum, relative, measurement error was estimated to be ±2%. The reproducibility of the experimental data, obtained at a given temperature, is about 0.8%.

No corrections for heat transfer by radiation in the substances that we investigated were introduced. The experimental results obtained on the temperature dependence of the thermal conductivity λ of the liquids investigated are presented in Table 1.