THE EXISTENCE OF THERMODYNAMIC CONSTANTS CHARACTERIZING THE PROPERTIES
OF SUBSTANCES AND MATERIALS IN SPONTANEOUS PROCESSES

V. N. Maslov

The equations of nonequilibrium thermodynamics show that one of the higher
time derivatives of the maximum thermodynamic work remains constant along
the trajectory of a spontaneous process. The theoretical prediction is con-
iming by experimental data on mechanical motion with friction. The constant
characterizing the friction process is called the coefficient of thermody-
namic friction losses (KTL). In contrast to the friction coefficient in mech-

nics, the KTL does not depend on the velocity and acceleration of relative
motion of parts of the frictional pair on the trajectory of spontaneous slow-
ing down. The KTL may be regarded as a nonequilibrium thermodynamic para-

meter specifying at a given temperature the properties of materials involved
in the friction process. The usefulness and advantages of utilizing the KTL
in engineering computations are noted.

It is well known that some specific parameters exist which are involved in the descrip-
tion of nonequilibrium states and processes [1]. Such are, for example, relaxation times,
excited state concentrations, and temperature and concentration gradients. In contrast to the
thermodynamic parameters of the equilibrium state, these variable parameters are explicit
functions of time or of time derivatives due to the fundamental nature of nonequilibrium
states which vary with time.

One may assume that there also exist some constants that characterize the nonequilib-
rium thermodynamic properties of substances and materials during spontaneous dissipative
processes. An argument in favor of this assumption are those experimental data on the de-
crease in the work capacity of nonequilibrium systems in dissipative chemical [2] and mech-
anical [3] processes that have been treated by using the equations of nonequilibrium thermo-
dynamics [4-6]. It was found that the value of one of the higher time derivatives remains
constant along the trajectory of the spontaneous process.

The purpose of the present paper is to emphasize that the thermodynamic constants of
this class possess some advantages over the conventional friction coefficient when describ-
ing the properties of substances and materials in mechanical processes with friction.

In nonequilibrium thermodynamics, spontaneous processes are regarded as inertial pro-
cesses in the sense that they can occur without the participation of external forces; the
thermodynamics also establishes the existence of two thermodynamic functions of state which
characterize the degree of deviation from equilibrium in accordance with the magnitude of
energy dissipation ($\dot{\Phi}$) and of the duration of the spontaneous process ($\tau$). The thermody-
namic potential $\Phi$ of a nonequilibrium state is defined by the minimized loss of the work
capacity of a system in a spontaneous process:

$$-\Delta \Phi = A_{\text{max}} - A,$$

where $-\Delta \Phi = \Phi - \Phi_{\text{eq}}$; $A_{\text{max}}$ is the maximum work that can be done in the equilibrium process;
$A$ is the characteristic work capacity in the spontaneous process. In many cases one can
use the normalization $\Phi_{\text{eq}} = 0$.

The physical meaning of the thermodynamic time $\tau$ is that it is the time interval be-
 tween the given nonequilibrium state and equilibrium state,
\[ \tau = \pm (t_{eq} - t), \quad 0 \leq \tau < +\infty, \] (2)

where \( t_{eq} \) is the time equilibrium attained in the laboratory time frame \( t \). The sign + or - depends on the choice of direction of the laboratory time \( t \).

For the implicitly prescribed function \( F[\psi, \tau, \dot{\psi}, \ddot{\psi} \ldots \phi^{(n)}] = 0 \), where the dots denote differentiation with respect to the thermodynamic time, the particular solution

\[ -\Delta \Phi = \frac{\Phi^{(n+1)}}{(n+1)!} \left. \tau^{n+1} \right|_{\phi^{(n+1)}=\text{const}}, \] (3)

has been obtained which is found to be valid for a quantitative description of spontaneous processes in systems of various physicochemical nature. The proper parameter \( n = 1, 2, \ldots \) has been called the dissipative order of the spontaneous process trajectory.

It has been shown in [3] how one can go over to the experimentally measurable quantities by means of the relation

\[ -\Delta \Phi = \alpha \cdot A_{\text{max}}^{n+1}, \] (4)

where \( \alpha \) is the dissipation coefficient, and \( \alpha = n/(n + 2) = \text{const} \) on that part of the spontaneous process trajectory where \( n = \text{const} \).

With the normalization \( \psi_{eq} = 0 \) and applying Eq. (4), we transform (3) to

\[ A_{\text{max}}^{n+1} = \frac{A_{\text{max}}^{(n+1)}}{(n+1)!} \tau^{n+1}. \] (5)

In mechanical systems

\[ A_{\text{max}} = K + \Pi, \] (6)

where \( K \) and \( \Pi \) are the kinetic and potential energies, respectively. Let us consider the simplest case of translational motion with sliding friction and \( \Pi = 0 \). Equation (5) can then be written as

\[ K = m \cdot v^2 = f \cdot \tau^{n+1}, \] (7)

where \( m \) is the mass and \( v \) the translational motion velocity. The quantity \( f = K^{(n+1)}/(n + 1)! \) is a constant that characterizes the spontaneous deceleration process in the case of motion with friction and may be termed the coefficient of thermodynamic friction losses.

As an example, we consider the experimental data on slowing down of a flywheel due to friction in the sliding bearings [3]. Semifluid friction is assumed and static friction will be neglected. Rotational motion is characterized only by the kinetic energy \( K = J \cdot \omega^2/2 \), where \( J \) is the moment of inertia and \( \omega \) is the angular velocity; there is no potential energy. An analysis of the experimental data showed that in the range of angular velocities studied, viz., between 10 and 1 rps, the spontaneous deceleration curve with a very high accuracy can be described by the equation

\[ \frac{J \cdot \omega^2}{2} = f \cdot \tau^4, \] (8)

where \( \tau = (68.1 - t) \, \text{sec} \) and \( f = 2.35 \cdot 10^{-6} \, \text{J} \cdot \text{sec}^{-4} \).

Like any other thermodynamic method, the thermodynamics of nonequilibrium states does not permit one to predict theoretically the numerical value of the coefficients. It is therefore not possible to determine thermodynamically the value of the coefficient \( f \) and its dependence on the nature of the frictional pair, composition of the lubricant, temperature, and other factors. These dependences must be established by special experiments or calculated on the basis of molecular-kinetic models.

In order to ascertain the possibility and expediency of using the coefficient of thermodynamic friction losses \( f \) in engineering computations with the aim of determining and minimizing energy losses due to friction and of characterizing the properties of the frictional pair materials or lubricants, let us find the relation between \( f \) and the friction coefficient \( \mu \) in the Amanton friction law,