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

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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 confirmed by experimental data on mechanical motion with friction. The constant characterizing the friction process is called the coefficient of thermodynamic friction losses (KTL). In contrast to the friction coefficient in mechanics, the KTL does not depend on the velocity and acceleration of relative motion of parts of the frictional pair on the trajectory of spontaneous slowing down. The KTL may be regarded as a nonequilibrium thermodynamic parameter 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 description 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 nonequilibrium thermodynamic properties of substances and materials during spontaneous dissipative processes. An argument in favor of this assumption are those experimental data on the decrease in the work capacity of nonequilibrium systems in dissipative chemical [2] and mechanical [3] processes that have been treated by using the equations of nonequilibrium thermodynamics [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 describing the properties of substances and materials in mechanical processes with friction.

In nonequilibrium thermodynamics, spontaneous processes are regarded as inertial processes 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 (Φ) and of the duration of the spontaneous process (τ). The thermodynamic potential Φ 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 τ is that it is the time interval between the given nonequilibrium state and equilibrium state,
\[ \tau = \pm (t_{eq} - t), \quad 0 \leq \tau < +\infty, \]  

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

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

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

\[ -\Delta \Phi = \alpha \cdot A_{\text{max}}, \]  

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 \( \phi_{eq} = 0 \) and applying Eq. (4), we transform (3) to

\[ A_{\text{max}} = \frac{A^{(n+1)}_{\text{max}} \tau^{n+1}}{(n+1)!}, \]  

In mechanical systems

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

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

\[ K = \frac{m \cdot \sigma^2}{2} = f \cdot \tau^{n+1}, \]  

where \( m \) is the mass and \( \sigma \) 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

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

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

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,