Markovian Description of Irreversible Processes and the Time Randomization (*).

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Summary. — A certain class of kinetic equations, which describe the Markov-type irreversible evolution of the system, consistent with the second law of thermodynamics and with the relaxation postulate, has been distinguished. The physical meaning of these kinetic equations is that they describe thermally activated processes. The time asymmetry, observed on the macrolevel as the thermodynamical irreversibility of the process, is represented on the microlevel by the Markov-type randomization of the moments of the jump-like change of the microstates of the system. As an example, the thermodynamical interpretation of the one-particle stochastic model of the many-body system is discussed.

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1. - Introduction.

In the theory of thermally activated processes one usually describes the rate of the process by means of the Arrhenius law[1, 2]. However, the kinetic theory based on the Arrhenius law has not been discussed in the literature. One of the purposes of this paper is to discuss such a theory, which is obtained by inserting the Arrhenius formula into the collision rates of the kinetic equation. We show that the kinetic equations obtained in that manner are consistent with the second law of thermodynamics, but exhibit an important difference compared with classical theory: in the classical kinetic theory the entropy increases along the solutions of the kinetic equation, whereas in our case the irreversibility is described by the fact that the free energy decreases in time.

The second and more fundamental purpose of this paper is to show how does the Arrhenius law occur naturally, as a result of a discussion of relations between the

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principles of thermodynamics and the structure of evolution described by a Markov process. From everyday experience and from phenomenological physics we know that macroscopic systems relax to the state of thermodynamical equilibrium according to the principles of thermodynamics. This general observation does not specify which mathematical model describes the time evolution of a physical system. In this paper we shall consider such systems, the time evolution of which is described by such Markov processes whose behaviour is consistent with the principles of thermodynamics. This leads to the notion of thermodynamically permitted Markov processes. A certain class of such processes, which describe the thermally activated phenomena, is introduced in sect. 4.

Before formulating a notion of a thermodynamically permitted Markov process, we shall shortly review some useful definitions. As is well known, the thermodynamical irreversibility is described by the second law of thermodynamics:

\[ dS = \delta_i S + \delta_e S, \quad \delta_i S \geq 0, \]

where \( dS \) is the total increment of the entropy \( S \), whereas \( \delta_e S \) and \( \delta_i S \) are its increments due to interaction of the system with the environment and due to the existence of irreversible processes in this system, respectively.

Usually, randomness of a state of a system is described by a probabilistic measure defined on the space of microstates, whereas the time evolution is described by the action of the one-parameter semi-group (which describes translations in time) in the space of measures. This evolution can be either «deterministic» or «random»; in this paper we shall discuss the case in which the randomness of microstate dynamics takes the form of a Markov process with values in the space of microstates \( X \). The probabilistic representation of microscopic description is then the so-called Markov semi-group; this semi-group is defined by the conditional probabilities of passing from one microstate to another (see sect. 2).

In order to compare the microscopic description with the thermodynamical description, one has to define the probabilistic representation of the state of the thermodynamical equilibrium relation

\[ F = E - \theta S, \]

between the free energy \( F \), the internal energy \( E \), the temperature \( \theta \) and the entropy \( S \).

Let us denote by \( D_\mu(X) \) the set of probabilistic measures on \( X \) which are specified by densities computed with respect to certain distinguished measure \( \mu \) on \( X \)

\[ D_\mu(X) = \left\{ f: X \to R, f \geq 0, \int_X f(x) \, d\mu(X) = 1 \right\}. \]

If every microstate \( x \in X \) has its own energy \( E_x \), then we can define the mean-energy functional

\[ E: D_\mu(X) \to R, \quad E(p) = \int_X e(x) p(x) \, d\mu(x), \quad e(x) = E_x \]

and we can distinguish the class of probabilistic measures giving the same value of