Thermally Stimulated Relaxation in Solids

Edited by P. Bräunlich

With Contributions by
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H. Glaefeke   P. Kelly   D. V. Lang   J. Vanderschueren

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Professor Dr. *Peter Bräunlich*

Department of Physics, Washington State University,
Pullman, WA 99164, USA

Preface

Thermally stimulated relaxation (TSR) by charge transport is only a small segment of the rich spectrum of solid-state processes which require an activation energy to proceed. This book deals specifically with electronic and ionic transport phenomena observed during nonisothermal temperature scans: thermoluminescence, thermally stimulated conductivity, thermally stimulated particle emission, and thermally stimulated depolarization. In selecting these topics we were guided by the need for critical appraisal of their utility as methods to obtain information on defects and impurities in nonmetals.

For historical reasons a number of loosely related phenomena are collectively called exoemission. Although only thermally stimulated exoemission of particles is of interest in the context of this volume, we choose to present it within the framework of all exoemission research.

The subjects are discussed on the basis of a mainly phenomenological or, at best, semiempirical theory of relaxation kinetics. Important applications in the dosimetry of ionizing radiation and in geological and archaeological research are described.

An enormous wealth of material on these topics has accumulated in the literature over the last three decades. A publication rate of over 500 per annum during the time this volume was prepared bears witness to a presently still very active field of research. Nevertheless, it appears to have reached a critical stage. Difficulties in unambiguous interpretation of experimental data have been recognized in recent years and a growing awareness has evolved of inherent limitations associated with most of the techniques for quantitative trap level spectroscopy.

This book was written to focus the attention of the specialists as well as the newcomers to the field onto these problems and to point out the need for novel experimental and theoretical approaches which fully utilize the potential of nonisothermal relaxation phenomena as investigative tools in solid-state physics.

Important first steps have already been taken. The development of junction capacitance spectroscopy for semiconductors is one example. Even though its most elegant experimental techniques do not require heating the sample according to a controlled heating program but rather are performed under isothermal conditions, in many cases rapid measurements can be made during a temperature scan and thus they resemble, at least formally, traditional thermally stimulated relaxation experiments.

Rather than writing a report on recent advances or a thorough review of experimental findings, we felt the purpose of this volume would best be served by choosing a largely tutorial style. Late developments, that for this reason could not be cited in the text (published mainly in 1977–1978), are listed in a bibliography.

Pullman, WA, August 1979   *P. Bräunlich*

Contributors

Bräunlich, Peter
    Department of Physics, Washington State University,
    Pullman, WA 99164, USA

DeWerd, Larry A.
    Departments of Radiology and Human Oncology,
    Medical Physics Division, 3321 Sterling Hall, University of Wisconsin,
    Madison, WI 53706, USA

Fillard, Jean-Pierre
    Université des Sciences et Techniques du Languedoc, Place E. Bataillon,
    F-34060 Montpellier Cedex, France

Gasiot, Jean
    Université des Sciences et Techniques du Languedoc, Place E. Bataillon,
    F-34060 Montpellier Cedex, France

Glaefeke, Harro
    Wilhelm-Pieck-Universität Rostock, Sektion Physik, Universitätsplatz 3,
    DDR-25 Rostock, German Democratic Republic

Kelly, Paul
    Division of Physics, National Research Council Ottawa,
    Ontario K1A OS1, Canada

Lang, David Vern
    Bell Laboratories, Murray Hill, NJ 07974, USA

Vanderschueren, Jacques
    Lab. de Chimie Physique, Université de Liège, Sart-Tilman,
    B-4000 Liège, Belgium

Contents

1. Introduction and Basic Principles

By P. Bräunlich

Two basic conditions have to be fulfilled for the occurrence of thermally stimulated relaxation (TSR) processes:

a) The system must be removed from statistical thermodynamic equilibrium and exist in a state which requires the reactants to surmount a free-energy barrier in order to move toward the reestablishment of equilibrium.

b) The system must be in contact with a temperature reservoir that provides the thermal energy necessary to activate the relaxation process.

Of interest for the study of thermally activated relaxation from a non-equilibrium steady-state situation back toward thermal equilibrium are therefore the ways to remove the system from equilibrium and the phenomena that can be measured or monitored during the relaxation process and thus utilized to characterize the occurring reactions. These processes encompass an enormous wealth of biological, chemical, and physical phenomena. Herein only those are considered which involve the redistribution over available energy states of electronic or ionic charge carriers in semiconducting and insulating solids during the relaxation process. Specifically selected are thermally stimulated charge transport and luminescence phenomena and thermally stimulated emission of charged particles from solid surfaces.

Theoretical descriptions of these phenomena are almost entirely based on the so-called absolute rate theory borrowed from chemical reaction kinetics [1.1]. Phenomenologically introduced reaction rates are determined experimentally on the basis of reasonable kinetic models.

1.1 Perturbation of the Thermodynamic Equilibrium

It is instructive to recall some of the fundamental relations of chemical reaction kinetics before we venture into the discussion of formally related phenomena in solid-state physics.

Consider the following reaction between ideal gases A, B, C, and D of concentrations n_A, n_B, n_C, and n_D:

$$A + B \leftrightarrow C + D. \tag{1.1}$$
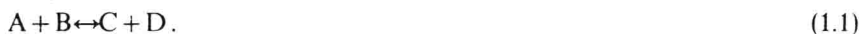
In thermodynamic equilibrium the law of mass action states

$$K \cdot n_A n_B = n_C n_D ;$$ (1.2)

K is the equilibrium constant given by

$$K = \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right).$$ (1.3)

ΔS is the change in entropy and ΔH the change in enthalpy. The entropy of the system is a measure of the total number of quantum states available to it. Thus, K is determined by the thermodynamic properties of the system which include the available energy levels and the temperature. Since $\Delta H - \Delta(TS) = \Delta G$, the change in standard Gibbs free energy, the equilibrium constant can be evaluated from a knowledge of the change in free energy and vice versa. This is one of the most powerful relations in the practical application of chemical thermodynamics.

The conditions to be fulfilled for the reestablishment of thermodynamic equilibrium of a system after perturbation is that the "path" between states is "sufficiently open". That is, once the system's equilibrium is perturbed, the return to equilibrium must be possible with a finite probability at $T \neq 0$. The processes occurring during the establishment of equilibrium in a perturbed system are the subject of interest in reaction chemistry which is concerned with the rate of chemical change and with the measurement of reaction rates to elucidate the mechanisms involved in the system's approach to thermodynamic equilibrium. These kinetic processes are not uniquely restricted to chemical reactions but also apply in quite precise analogy to such phenomena as thermal ionization of gases or defect states in solids, polarization or magnetization of materials, annealing of defects, diffusion and flash desorption, to mention just a few [1.9], and, therefore, it appears justified to apply the wealth of physical insight available from chemical kinetics to the subjects selected for the present volume.

Most of the answers to the question as to how much one can learn about a reaction from kinetic considerations alone have been given before by chemical kineticists. The following statement by *Noyes* [1.2] is as valid for electron kinetic reactions in solids as it is for chemical reactions:

"The *mechanism* of a chemical reaction is the detailed combination of reversible and irreversible elementary processes whose net consequence is the reaction of interest. Kinetic data furnish the most direct clues for discovering the mechanism in any specific example. However, in principle an infinite number of microscopic mechanisms can be proposed to explain any set of macroscopic observations. A molecular mechanism can never be proved in a rigorous sense, but kinetic measurements can often disprove a mechanism and show it is not consistent with observations. Confidence increases with the volume of data consistent with a simple interpretation. Mechanisms of a small but significant number of reactions now seem to be established beyond question."
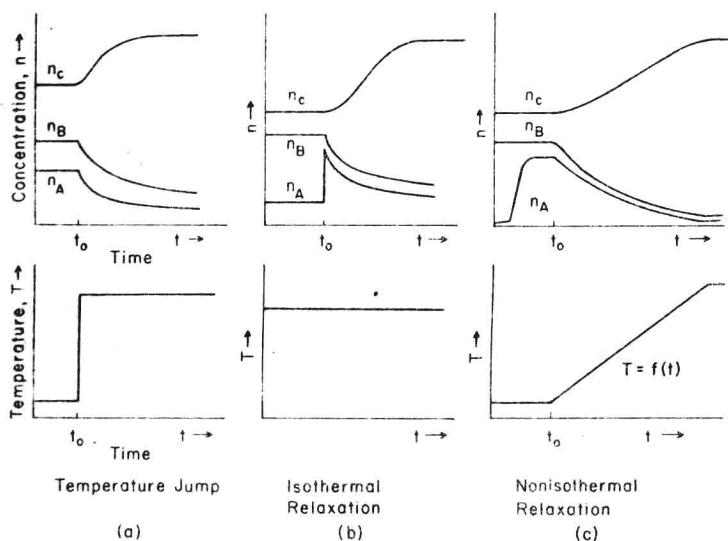
Fig. 1.1a–c. Relaxation of a system of reactants after perturbation of the thermodynamic equilibrium by a sudden increase in temperature (**a**), a sudden increase in the concentration of one reactant at a constant temperature (**b**), and an increase of the concentration of one reactant at a low temperature with subsequent linear temperature rise (**c**)

The equilibrium of a system may be perturbed by changing the concentration of the reactants, the temperature, pressure, electric or magnetic field (including electromagnetic fields), etc. (Fig. 1.1). The establishment of a new equilibrium condition during and after the perturbation may be monitored by the measurement of the concentration of the involved species and the results can be utilized for the study of the involved chemical or physical reactions. Since the temperature has, in the majority of cases, a most pronounced effect on the reaction rates, it has to be carefully controlled. Two basic types of relaxation techniques are used:

a) Isothermal relaxation: the perturbation is implemented at a constant temperature which is, whenever possible, selected to assure experimentally convenient relaxation times.

b) Nonisothermal relaxation: the system is perturbed at a sufficiently low temperature to reduce the probability to establish a new statistical equilibrium. Subsequently, the temperature is increased according to a well-controlled heating program $T(t)$, thus increasing the reactions rates and the relaxation of the system can be monitored as a function of temperature and time.

Technique a) is most successfully used not only in the study of chemical reactions [1.3, 4], but also in electronic reaction kinetics in solids [1.5–7], most notably in the recently developed technique of deep-level transient spectroscopy [1.8]. Nonisothermal relaxation is employed in the studies of thermally stimulated luminescence, conductivity, exoemission, polarization, and depolarization.

1.2 Formal Description of Kinetic Observations

The rate at which a perturbed system reacts during the relaxation process has frequently been described in a rather formal way, justified solely on the basis of an "acceptable" fit of experimental observations, by an equation of the form

$$\frac{d[n_D]}{dt} = \alpha[n_A]^m[n_B]^n[n_C]^l, \tag{1.4}$$

where n_D is the concentration of the product resulting from the reaction between the reactants n_A, n_B and n_C, and α is the so-called specific reaction rate constant or rate coefficient. A reaction of the form (1.4) is visualized as involving elementary processes, taking place in single steps, in which one, two or possibly more species of the reactants take part. These steps are called unimolecular, bimolecular, etc., and the reaction rates accordingly are said to be of first, second, third order and so on. The reaction of (1.4) is of m-th order in n_A, n-th order in n_B, and l-th order in n_C.

Sometimes it is possible to describe the change of the concentration of a reactant n_D by a simple equation of the form $d[n_D]/dt = \alpha[n_D]^l$, where $\alpha = v \exp(-E/kT)$, E is an activation energy, and v is the so-called frequency factor. This approach is justified whenever empirical data can be fitted by an Arrhenius equation.

Clearly, such a formal "order-kinetics" of the reaction or relaxation process is only a phenomenological description of measured rates that can be related to actually involved physical processes only in very simple cases (see Sect. 2.6.4) [1.9, 10]. The order of a process is an empirical quantity, the experimental determination of which does, in general, not permit an unequivocal interpretation of the details of the reaction. In addition, no reaction will obey (1.4) close to steady-state equilibrium when $d[n_D]/dt$ approaches zero despite the fact that neither any of the concentrations nor α is zero [1.2].

1.3 The Principle of Detailed Balance

Equation (1.4) applies only to systems that are far removed from thermal equilibrium so that the reaction essentially occurs only in one direction. It is assumed that only the product n_D is formed from the reaction of the reactants n_A, n_B and n_C. Eventually the reverse reaction, namely the decomposition of n_D into reactants, becomes more and more probable until the forward and reverse reaction are in a state of detailed balance.

This principle of detailed balance is a result of microscopic reversibility of chemical, electron kinetic and other reactions. It is prerequisite for the establishment of thermal equilibrium which requires that forward and reverse reaction rates are identical for every individual reaction path possible.

In essence, a reaction made possible at a temperature T by increasing the concentration of one or more reactants and thus removing the system from equilibrium, will continue until new concentrations of the reaction product and the reactants are established. If the reaction proceeds isothermally, the equilibrium constant is unchanged. In nonisothermal reactions it varies with T and an equilibrium is finally established in which all concentrations as well as K assume new values. The principle of detailed balance if of fundamental importance to establish helpful relations between reaction constants and equilibrium constants [1.11], since both at the initial thermal equilibrium and at the new equilibrium after the relaxation of the perturbation the net forward and reverse reaction rates are zero.

1.4 Theoretical Approaches to Reaction Kinetics

Kinetic theories of chemical and other (e.g., electronic recombination) reactions attempt to explain the rates at which the processes proceed and to describe their behavior as a function of such variables as temperature, time, and, of course, concentration of the reactants and products.

Two approaches toward theoretical interpretations of such reactions are taken:

I) It is attempted to describe the reaction in terms of elementary processes, the theory of which results in a rate equation with known cross sections for the elementary processes. The collision theories of simple bi- and mono-molecular gas reactions are examples [1.12, 13].

II) A statistical thermodynamic theory of absolute reaction rates is applied which assumes that the reaction is a continuous process and that the concentrations of the reactants as well as the products can be calculated by statistical methods. Characteristic for this theoretical approach is that one configuration, the activated complex or transition state, is crucial. Once it has been attained by passage through an energy barrier (activation energy), the probability for completion of the reaction is assumed to be large and, at the same time, the equilibrium (or better steady-state) distribution of the reactants capable of reaching this state is not disturbed. This then is precisely why in a nonisothermal experiment the heating rate must be sufficiently slow because otherwise statistical steady-state arguments cannot be used to calculate the ratio of the concentration of reactants in the transition state and any other of their possible energy states [1.14, 15].

Naturally, a complete theory of the reaction which provides a detailed description of the rate constant and the cross sections is preferable. However, it is available only for a few cases [1.12, 13]. The more prevalent situation is characterized by a number of possible microscopic mechanisms, such that all that is available for the interpretation is a set of different plausible phenomenological rate equations with unknown rate constants. Through statistical