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Kinetic Analysis by Chemical Relaxation Methods

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The significance of chemical relaxation experiments (e.g., temperature jump measurements) for kinetic investigations of reaction systems involving any degree of complexity is examined. On the basis of a general solution of the relaxation problem, the properties of experimentally measurable relaxation curves—characterized by a relaxation spectrum—are discussed. Usually, actual theoretical or experimental determinations of complete relaxation spectra and their use for kinetic analyses are practicable only for fairly simple reaction systems. In the case of more complex systems an evaluation of relaxation experiments in terms of mean relaxation times is suggested. The mean reciprocal relaxation time is of particular significance. This quantity is shown to be fairly easily accessible experimentally. On the other hand, it can be computed without a complete solution of the relaxation problem. Examples are given to demonstrate the procedure and its potentialities with respect to the investigation of complicated reaction processes.

I. INTRODUCTION

Relaxation methods have brought about substantial progress in the investigation of the kinetics of chemical reactions in solution.[1] Unlike classical experimental procedures, these techniques do not initiate the reaction process by mixing of the reaction partners—which would not allow measurements below 10^{-3} sec—but by perturbing a time-independent stationary state of the system, usually the chemical equilibrium. Such perturbations can be brought about in less than 10^{-9} sec. Since the time course of the induced chemical relaxation process can generally be followed by some means, very fast reactions may be studied in this way. Furthermore, if intermediate states and more than one elementary reaction step are involved, a spectrum of relaxation times will occur which provides much more information about the kinetics and mechanism than the rate of the over-all reaction determined by classical methods.

Generally, in order to describe the relaxation behavior by a relaxation spectrum, sufficiently small perturbations have to be applied. In this case the rate equations can be linearized so that they may be solved, in principle, by well-known mathematical operations. One finds the same number of relaxation times as there are linearly independent elementary steps involved in the system, each relaxation time depending in a more or less complicated manner on the rate constants of all the elementary processes as well as on the concentrations of the reaction partners.

During the past ten years, a number of relaxation techniques have been developed and very successfully employed in the study of numerous fast reactions in solution. Temperature jump techniques—for relaxation times from 10^{-6} to 1 sec—and ultrasonic absorption methods—suitable in the time range 10^{-9} to 10^{-6} sec—have proved to be of particular versatility.[1]

Almost all the reaction systems investigated so far by relaxation experiments have been relatively simple, i.e., there was only one relaxation time (i.e., only one reaction step), or else the spectrum consisted of a few relaxation times differing considerably in their magnitude. In such cases the relaxation spectrum can be determined experimentally without great difficulties, and the necessary theoretical calculations can be carried out quite readily. Unfortunately, the situation becomes much more unfavorable if more complex reactions involving a greater number of elementary processes are to be studied. Then, actual calculations of the relaxation spectrum will usually be extremely tedious—even with the help of a computer—or not practicable at all. Under these circumstances, an experimental determination of the complete spectrum is generally not feasible. Nevertheless, there are, of course, numerous reactions of the more complicated type which are of interest, particularly as far as processes of biological significance are concerned (e.g., conformation changes of biopolymers[2–6]). Thus the question arises, what can actually be measured in such cases by relaxation methods? What quantities are accessible experimentally even if the complete relaxation spectrum cannot be determined? Can such quantities eventually be calculated theoretically and interpreted in terms of the reaction mechanism without a solution of the complete relaxation problem?

This article deals with these problems. The chemical relaxation of a reaction system comprising an arbitrary number of elementary reaction steps is reviewed first from a general point of view. Although the theory has been discussed already in the literature in various aspects,[1,7,8] a very general but compact representation of its essentials is given here in order to lay the necessary foundations of the considerations in the following sections. The calculations require some knowledge of matrix algebra. It is strongly recommended that one acquires this knowledge if one is seriously interested in the analysis of chemical relaxation data. However,

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for the present, the following calculations are not absolute prerequisites for the discussion later on and may be skipped if one is interested only in the results. Subsequent to the basic introduction, the properties of experimentally observable relaxation curves are investigated, especially for the practically important cases of stepwise and periodical perturbations of a stationary state (e.g., due to temperature jumps or ultrasonic waves, respectively). Evaluation of the complete relaxation spectrum from such a curve provides a maximum of information from one experiment which may be utilized for a kinetic analysis of the reaction system. This involves difficulties which are not readily surmountable if the underlying reaction mechanism is too complicated. It is shown, however, that even under these circumstances certain mean relaxation times can be determined from the experiments. They may be used for kinetic interpretations. Since those mean values do not reflect as much information as a complete relaxation spectrum, more pertinent experiments are necessary.

The mean reciprocal relaxation time proves to be of particular importance. This quantity is related to the initial rate of the relaxation process taking place after a stepwise perturbation. It can be determined fairly easily even for rather complex reaction systems—experimentally as well as theoretically. Knowledge of the complete relaxation spectrum is not required. After a general treatment, examples are given to demonstrate the procedure of calculation and the significance of the results with respect to kinetic analyses. The analysis in terms of mean relaxation times—as discussed in this article for chemical relaxation—can be extended analogously to any other relaxation process.

II. GENERAL THEORY OF CHEMICAL RELAXATION

Reaction System

The general case of a chemical reaction system may comprise n elementary processes involving m different reaction partners A_i $(i=1, 2, \cdots, m)$. The elementary reactions can usually be expected to be unimolecular or bimolecular. However, in order to include all types of reactions, we describe them in the most general way:

$$\nu_{s1}A_1+\nu_{s2}A_2+\cdots\nu_{sm}A_m \underset{k_s'}{\overset{k_s}{\rightleftharpoons}} \nu_{s1}'A_1+\nu_{s2}'A_2+\cdots\nu_{sm}'A_m. \quad (1)$$

$(s=1, 2, \cdots, n)$. Normally, only a few of the stoichiometric coefficients ν and ν' are different from zero as far as a special reaction is concerned. A substance A_i catalyzing the process may appear on both sides. The rate constants of the forward and reverse reactions are denoted by k_s and k_s', respectively. Then, according to the principles of reaction kinetics, the corresponding elementary rates of reaction are

$$v_s=(\nu_{si}'-\nu_{si})^{-1}(dc_i/dt)_s=k_s c_1^{\nu s1}c_2^{\nu s2}\cdots c_m^{\nu sm},$$

$$v_s'=(\nu_{si}-\nu_{si}')^{-1}(dc_i/dt)_s'=k_s' c_1^{\nu' s1}c_2^{\nu' s2}\cdots c_m^{\nu' sm}. \quad (2)$$

The c_i are the concentrations of the A_i. The differential quotients stand for the temporal rates of change of any c_i due to the special reaction in view (number s, forward or reverse). This is meaningful only for those A_i which are actually converted $(\nu_{si}\neq\nu_{si}')$.

Summing up the effects of all the elementary processes yields the total change of c_i:

$$dc_i/dt=\sum_s (\nu_{si}'-\nu_{si})(v_s-v_s') \qquad (i=1, 2, \cdots, m). \quad (3)$$

Thus a set of differential equations is obtained which describes the kinetic behavior of the reaction system. In the absence of external effects, the system approaches the state of chemical equilibrium as determined by its thermodynamic properties. By appropriate external means, however, some other stationary state may be maintained. For any stationary state we have $dc_i/dt=0$, i.e., the respective concentrations constitute a time-independent solution of (3). Consequently the sum (3) has to be zero. In the special case of chemical equilibrium, each single term of it must vanish, i.e., the equilibrium values of the elementary rates $\bar{v}_s$ and $\bar{v}_s'$ are equal for any individual elementary process:

$$\bar{v}_s=\bar{v}_s', \quad (4a)$$

or, because of (2),

$$[(\bar{c}_1^{\nu' s1}\bar{c}_2^{\nu' s2}\cdots\bar{c}_m^{\nu' sm})/(\bar{c}_1^{\nu s1}\bar{c}_2^{\nu s2}\cdots\bar{c}_m^{\nu sm})]=k_s/k_s'=K_s. \quad (4b)$$

($\bar{c}_i$ are equilibrium concentrations.) Accordingly, if chemical equilibrium is attained for the over-all reaction, it is established also for each elementary process. K_s means the respective elementary equilibrium constant. [Strictly speaking, this holds true for dilute solutions only; yet relation (4b) remains formally correct under any conditions if K_s is taken as an apparent equilibrium constant which is pertinently composed of the true equilibrium constant and the activity coefficients of the reaction partners.] The above expressions (4a, b)—known as "principle of detailed balance"[9]—cannot be derived from ordinary classical thermodynamics, but are a consequence of the more general "principle of microscopic reversibility."[10,11]

A solution of the Eqs. (3) may be extremely difficult even for fairly simple systems, especially if nonlinearities are introduced either by elementary reactions of higher than the first order or by time dependent rate constants (due to change of the temporary equilibrium state). Nevertheless, the general

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rate equations can always be linearized and solved in principle if they are applied to chemical relaxation processes caused by sufficiently small perturbations of the chemical equilibrium or some other stationary state which is maintained by external means.

The Relaxation Equations

First we introduce some set of time-independent reference concentrations c_i^0 $(i=1, 2, \cdots, m)$. Then $\gamma_i = c_i - c_i^0$, $\bar{\gamma}_i = \bar{c}_i - c_i^0$ may describe the deviations of the actual concentrations c_i and the stationary state concentrations $\bar{c}_i$ from the reference values. The net rate of an elementary process $v_s - v_s'$ is expanded in a Taylor series about the stationary state, yielding a power series in the quantities $c_j - \bar{c}_j = \gamma_j - \bar{\gamma}_j$. Terms higher than the first order are neglected, assuming the deviations to be sufficiently small $(\gamma_j - \bar{\gamma}_j \ll \bar{c}_j)$. The factor of $\gamma_j - \bar{\gamma}_j$ can be evaluated using the Eq. (2). The condition of stationarity requires that the total rate of change $dc_i/dt = d\gamma_i/dt$ vanish for $\gamma_i = \bar{\gamma}_i$. Thus, by inserting the linearized elementary rates into (3), the general rate equations turn into a set of differential equations which are linear with respect to $\gamma_j - \bar{\gamma}_j$:

$$d\gamma_i/dt = \sum_j a_{ij}(\gamma_j - \bar{\gamma}_j), \tag{5a}$$

where

$$a_{ij} = -\sum_s (\nu_{si} - \nu_{si}')[(\nu_{sj}\bar{v}_s - \nu_{sj}'\bar{v}_s')/\bar{c}_j]. \tag{5b}$$

Since the temporary stationary state may still be a function of time, the quantities $\bar{v}_s$, $\bar{v}_s'$, $\bar{c}_j$, and, consequently, the coefficients a_{ij} are not necessarily constants. However, under the assumption of small deviations from the reference state, i.e., for

$$|\gamma_j|, |\bar{\gamma}_j| \ll c_j^0 \approx \bar{c}_j, \tag{5c}$$

this effect produces only small variations of the second order. Thus they may be neglected and the a_{ij} assumed to be independent of time.

If the chemical relaxation takes place towards chemical equilibrium—as is frequently the case in practical applications—the coefficients a_{ij} of the relaxation equations (5a) can be somewhat simplified by means of the "principle of detailed balance." Due to (4a) we have

$$a_{ij} = -\sum_s (\nu_{si} - \nu_{si}')(\nu_{sj} - \nu_{sj}')(\bar{v}_s/\bar{c}_j). \tag{5d}$$

The General Solution of the Relaxation Equations

In principle, the relaxation equations (5a) can be solved by means of standard mathematical procedures. For this purpose it is suitable to employ matrix algebra. Let us define first the matrix

$$\mathbf{A} = (a_{ij}) \qquad (i, j = 1, 2, \cdots, m) \tag{6}$$

as well as the column vectors

$$\boldsymbol{\gamma} = (\gamma_1, \gamma_2, \cdots, \gamma_m)^\dagger, \qquad \bar{\boldsymbol{\gamma}} = (\bar{\gamma}_1, \bar{\gamma}_2, \cdots, \bar{\gamma}_m)^\dagger \tag{7}$$

(which are written as transposed row vectors using the conventional superscript †). Then the relaxation equations (5a) can be simply expressed as

$$\dot{\boldsymbol{\gamma}} = \mathbf{A}(\boldsymbol{\gamma} - \bar{\boldsymbol{\gamma}}). \tag{8}$$

(The dot indicates differentiation with respect to time).

In the case of relaxation about chemical equilibrium the diagonal matrix $\mathbf{G} = [\delta_{ij}/(\bar{c}_i)^{1/2}]$ (with Kronecker's δ symbol equal to unity for $i=j$ and equal to zero otherwise) may be used to introduce a new matrix

$$\mathbf{A}' = \mathbf{G}\mathbf{A}\mathbf{G}^{-1}. \tag{9a}$$

Taking Eq. (5d) into account its elements turn out to be

$$\begin{aligned} a_{ij}' &= [(\bar{c}_j)^{1/2}/(\bar{c}_i)^{1/2}]a_{ij} \\ &= -\sum_s (\nu_{si} - \nu_{si}')(\nu_{sj} - \nu_{sj}')[\bar{v}_s/(\bar{c}_i\bar{c}_j)^{1/2}] = a_{ji}'. \end{aligned} \tag{9b}$$

Consequently $\mathbf{A}'$ is a symmetric matrix. For this reason—as is well known from linear algebra—there exist precisely m linearly independent orthogonal and normalized eigenvectors $\mathbf{x}_r'$ with respective real (i.e., noncomplex) eigenvalues λ_r satisfying the equations

$$\lambda_r\mathbf{x}_r' = \mathbf{A}'\mathbf{x}_r' \qquad (\text{where } \mathbf{x}_r'^\dagger\mathbf{x}_s' = \delta_{rs}). \tag{10}$$

Now two more linearly independent sets of vectors may be defined:

$$\mathbf{x}_r = \mathbf{G}^{-1}\mathbf{x}_r', \qquad \mathbf{y}_r = \mathbf{G}\mathbf{x}_r'. \tag{11a}$$

It follows from (10) and (11a) that

$$\lambda_r\mathbf{x}_r = \mathbf{A}\mathbf{x}_r, \qquad \lambda_r\mathbf{y}_r^\dagger = \mathbf{y}_r^\dagger\mathbf{A}. \tag{11b}$$

Thus, in the case of the generally nonsymmetric matrix $\mathbf{A}$, the vectors $\mathbf{x}_r$ and $\mathbf{y}_r^\dagger$ form a set of column and row eigenvectors, respectively. Because of the orthogonalization and normalization of the $\mathbf{x}_r'$, we have

$$\mathbf{y}_r^\dagger\mathbf{x}_s = \delta_{rs}. \tag{11c}$$

The eigenvalues λ_r remain the same as for $\mathbf{A}'$. They may be obtained as the roots of the characteristic equation

$$|\mathbf{A} - \lambda\mathbf{E}| = 0, \tag{12}$$

($\mathbf{E}$ being the unity matrix and $|\mathbf{A} - \lambda\mathbf{E}|$ being the determinant of the enclosed matrix,) which is an algebraic equation of the mth order.

It has been assumed so far that $\mathbf{A}$ describes relaxation towards chemical equilibrium. As a matter of fact, eigenvalues can be computed for any matrix $\mathbf{A}$ by means of Eq. (12). Usually the respective sets of eigenvectors according to Eqs. (11b, c) exist also (e.g., if all the eigenvalues are different from each other). Therefore the mathematical procedure pointed out here can generally be applied to relaxation processes occuring after small perturbations of any stationary state. However, complex eigenvalues can be excluded only for chemical equilibrium. In the case of other stationary states, the "principle of detailed balance" cannot be used; then the relaxation matrix cannot be symmetrized according to (9a, b).

Now the general solution of the relaxation equation (8) may be obtained in the following way: We represent the vector in demand, $\boldsymbol{\gamma}$, as well as the vector of the respective temporary equilibrium values, $\bar{\boldsymbol{\gamma}}$, by a linear combination of the eigenvectors $\mathbf{x}_r$, i.e., we set

$$\boldsymbol{\gamma}=\sum_r \alpha_r \mathbf{x}_r, \qquad \bar{\boldsymbol{\gamma}}=\sum_r \bar{\alpha}_r \mathbf{x}_r. \tag{13a}$$

This is always possible because of the linear independence of the $\mathbf{x}_r$. It follows immediately from (11c) that

$$\alpha_r=\mathbf{y}_r^{\dagger}\boldsymbol{\gamma}, \qquad \bar{\alpha}_r=\mathbf{y}_r^{\dagger}\bar{\boldsymbol{\gamma}}. \tag{13b}$$

Equations (13a) describe a coordinate transformation. The new coordinates α_r and $\bar{\alpha}_r$, respectively, are called normal coordinates (or normal variables). They may be used to build up the two column vectors

$$\boldsymbol{\alpha}=(\alpha_1, \alpha_2, \cdots, \alpha_m)^{\dagger}, \qquad \bar{\boldsymbol{\alpha}}=(\bar{\alpha}_1, \bar{\alpha}_2, \cdots, \bar{\alpha}_m)^{\dagger}. \tag{14}$$

Then (13a) can be written in the alternative form

$$\boldsymbol{\gamma}=\mathbf{M}\boldsymbol{\alpha}, \qquad \bar{\boldsymbol{\gamma}}=\mathbf{M}\bar{\boldsymbol{\alpha}}, \tag{15a}$$

where the transformation matrix $\mathbf{M}$ and its inverse $\mathbf{M}^{-1}$ read:

$$\mathbf{M}=(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_m), \qquad \mathbf{M}^{-1}=(\mathbf{y}_1, \mathbf{y}_2, \cdots, \mathbf{y}_m)^{\dagger}. \tag{15b}$$

[This representation of $\mathbf{M}^{-1}$ is readily verified by means of the relations (11c).] If we insert (13a) into (8) and take into account (11b), the relaxation equations become

$$\sum \dot{\alpha}_r \mathbf{x}_r=\sum (\alpha_r-\bar{\alpha}_r)\,\mathbf{A}\mathbf{x}_r=\sum \lambda_r(\alpha_r-\bar{\alpha}_r)\mathbf{x}_r. \tag{16}$$

Since the $\mathbf{x}_r$ are linearly independent, the individual terms of these sums must be equal to each other separately. After having introduced the relaxation times

$$\tau_r=-(\lambda_r)^{-1} \tag{17}$$

for any $\lambda_r \neq 0$, we find that

$$\dot{\alpha}_r=-(\alpha_r-\bar{\alpha}_r)/\tau_r \text{ (for } \lambda_r\neq 0), \qquad \dot{\alpha}_r=0 \text{ (for } \lambda_r=0). \tag{18}$$

Thus the relaxation equations are particularly simple if formulated in terms of normal variables. This is due to the fact that $\mathbf{M}$ and $\mathbf{M}^{-1}$ transform $\mathbf{A}$ to a diagonal matrix of the eigenvalues: $\mathbf{M}^{-1}\mathbf{A}\mathbf{M}=(\lambda_i\delta_{ij})$. According to (18), a zero eigenvalue results in a constant (time-independent) normal coordinate α_r. Since the α_r are linear functions of the original concentration variables γ_i, this means a relation of linear dependence for these γ_i. Vice versa, any such linear dependence results in a zero eigenvalue. This occurs, for instance, as a consequence of conditions imposed one the system due to mass conservation. At least one such relation must exist in a closed system, so the number of zero eigenvalues m_0 satisfies the inequalities $1 \leq m_0 < m$. It is advisible, especially for actual calculations, to eliminate m_0 concentration variables appearing in the relaxation equations (5a) [or (8), respectively] together with the corresponding differential equations by taking advantage of the m_0 linear dependences. Then the original set of equations is reduced to a formally simpler system of only $m-m_0$ linear differential equations. This system can be treated and solved in the same manner as above. The $m-m_0$ eigenvalues will be identical with the nonzero eigenvalues of the original system. For this reason one may always assume the relaxation equations to be of the reduced type with no zero eigenvalues.

The general solution of the relaxation problem is easily obtained by evaluation of (18). For any set of time-dependent $\bar{\alpha}_r(t)$, the α_r are found to be

$$\alpha_r=\exp(-t/\tau_r)\int [\exp(t/\tau_r)/\tau_r]\bar{\alpha}_r(t)\,dt. \tag{19}$$

The as-yet undetermined integration constant of the indefinite integral has to be fixed in compliance with the boundary conditions of the special problem in consideration. A representation of (19) in terms of the original concentration vectors $\boldsymbol{\gamma}$ and $\bar{\boldsymbol{\gamma}}$ may be given using the matrices

$$\begin{aligned}\mathbf{T}(t)&=\mathbf{M}\mathbf{R}(t)\\ &=[\exp(-t/\tau_1)\mathbf{x}_1, \exp(-t/\tau_2)\mathbf{x}_2, \cdots],\\ \mathbf{T}^{-1}(t)&=\mathbf{R}^{-1}(t)\cdot\mathbf{M}^{-1}\\ &=[\exp(t/\tau_1)\mathbf{y}_1, \exp(t/\tau_2)\mathbf{y}_2, \cdots]^{\dagger},\end{aligned} \tag{20}$$

where $\mathbf{R}(t)=[\exp(-t/\tau_i)\cdot\delta_{ij}]$ is a diagonal matrix.

The relations (19) can be written as

$$\boldsymbol{\gamma}=-\mathbf{T}\int \mathbf{T}^{-1}\mathbf{A}\bar{\boldsymbol{\gamma}}\,dt. \tag{21}$$

This is the general solution of the relaxation equation (8). The matrix $\mathbf{T}$ satisfies the homogenous differential equation $\mathbf{T}=\mathbf{A}\mathbf{T}$. Any other solution, i.e., any $\mathbf{T}'=\mathbf{T}\mathbf{C}$ with a constant matrix $\mathbf{C}$, could be used in (21) instead of $\mathbf{T}$, as can be easily verified by inserting (21) into (18).

Summary of the Mathematical Analysis

The various steps in the mathematical analysis of a given relaxation problem may be summarized. First, the relaxation equations as represented in (5a) must be established by linearizing the kinetic rate equations. Linear dependences (e.g., due to mass conservation) should be eliminated in order to reduce the number of variables as much as possible. Then the eigenvalues of the relaxation matrix $\mathbf{A}$ [Eq. (6)], i.e., the roots of its characteristic equation (12), have to be evaluated resulting in the relaxation times of the system according to (17). Once the eigenvalues are known, the eigenvectors $\mathbf{x}_r$ and $\mathbf{y}_r^\dagger$ can be obtained by solving the sets of linear equations (11b). The eigenvectors have to be normalized so that they satisfy the relation (11c). After that the transformation matrices $\mathbf{M}$ and $\mathbf{M}^{-1}$ [Eqs. (15b)] can easily be written down. Application of (19 or (21) yields the solution of the given problem if the special boundary conditions are used to determine the integration constants.

In principle, the computational procedure described above may be used in any case. Its practical applicability, however, is restricted to systems where the eigenvalues and eigenvectors of their matrix $\mathbf{A}$ can be calculated with reasonable effort (a computer may be necessary). The method is generally not practicable for high-order matrices, i.e., for systems with a greater number of independent elementary reactions.

Special Solutions of the Relaxation Equations

Two cases of relaxation problems are of particular importance with respect to experimental applications:

(a) Approach to a constant stationary state (e.g., the process of equilibration after a temperature jump).

The stationary state to be approached may not change for $t \geq 0$. If this state is taken as the reference, we have $\bar{\gamma}_r = \bar{\alpha}_r = 0$ for any r. Then Eq. (19) easily yields

$$\alpha_r = \mathring{\alpha}_r \cdot \exp(-t/\tau_r), \qquad (22a)$$

where $\mathring{\alpha}_r$ denotes the value of α_r at $t=0$.

(b) Periodic variations of a temporary stationary state (e.g., due to pressure or temperature oscillations caused by sound waves).

In the case of harmonic oscillations of angular frequency ω, the stationary state values $\bar{\gamma}_j$ and $\bar{\alpha}_r$ may be represented by $\bar{\gamma}_j = \mathring{\gamma}_j \exp(i\omega t)$ and $\bar{\alpha}_r = \mathring{\alpha}_r \exp(i\omega t)$, respectively, $\mathring{\gamma}_j$ and $\mathring{\alpha}_r$ being the amplitudes. Under these conditions (19) leads to

$$\alpha_r = \mathring{\alpha}_r/(1+i\omega\tau_r) \cdot \exp(i\omega t) = \bar{\alpha}_r/(1+i\omega\tau_r). \qquad (22b)$$

With $\mathring{\boldsymbol{\alpha}}$ being a column vector made up by the $\mathring{\alpha}_r$, the original concentration variables are readily obtained employing (13a) or (15a):

$$\boldsymbol{\gamma} = \mathbf{MR}\mathring{\boldsymbol{\alpha}} = \sum_r \mathring{\alpha}_r \cdot \exp(-t/\tau_r) \cdot \mathbf{x}_r \qquad (23a)$$

if a constant stationary state is approached, and

$$\boldsymbol{\gamma} = \sum_r [\mathring{\alpha}_r/(1+i\omega\tau_r)] \cdot \exp(i\omega t) \cdot \mathbf{x}_r \qquad (23b)$$
$$= \sum_r [\bar{\alpha}_r/(1+i\omega\tau_r)] \cdot \mathbf{x}_r$$

for harmonic oscillations of a temporary stationary state. The deviations of the concentrations from their stationary state values at $t=0$ or the amplitudes of the periodical variations of stationary state concentrations, respectively, are given by

$$\mathring{\boldsymbol{\gamma}} = \mathbf{M}\mathring{\boldsymbol{\alpha}} = \sum_r \mathring{\alpha}_r \mathbf{x}_r. \qquad (24a)$$

These boundary conditions determine the factors $\mathring{\alpha}_r$ for the special problem under consideration. We find

$$\mathring{\boldsymbol{\alpha}} = \mathbf{M}^{-1} \cdot \mathring{\boldsymbol{\gamma}}, \qquad \text{i.e., } \mathring{\alpha}_r = \mathbf{y}_r^\dagger \cdot \mathring{\boldsymbol{\gamma}}. \qquad (24b)$$

III. GENERAL PROPERTIES OF EXPERIMENTAL RELAXATION CURVES

Relaxation Functions

Chemical relaxation of a reaction system is followed experimentally by measuring some appropriate quantity which responds to the changes of concentrations of the reaction partners. Frequently such a measurable quantity (e.g., optical density) may be represented as a linear function of the concentrations. Otherwise it can be linearized at least in the vicinity of a reference state by means of a Taylor expansion. There the deviation of a given measurable quantity (or observable) P from its reference value $P^0 = P(c_1^0, c_2^0, \cdots,)$ may be written generally as

$$\delta P = P - P^0,$$
$$= \sum_j (\partial P/\partial\gamma_j)_{\gamma_i=0} \cdot \gamma_j,$$
$$= \sum_r (\partial P/\partial\alpha_r)_{\alpha_i=0} \cdot \alpha_r, \qquad (25)$$

[where $(\partial P/\partial\gamma_j)_{\gamma_i=0} = (\partial P/\partial c_j)_{c_i=c_i^0}$]. The experimentally measurable change of δP during a relaxation process is readily obtained by substituting the respective solutions of the relaxation equations for the γ_j or α_r.

Let us consider the two special relaxation processes discussed above. If the stationary state is constant for $t \geq 0$, it may be taken as the reference state. The deviation of P from $P^0 = \bar{P}$ may be equal to δP_0 at $t=0$. The decay of δP is then described by

$$\delta P = \Phi(t) \cdot \delta P_0, \qquad (t \geq 0), \qquad (26a)$$

thus defining a pertinent relaxation function $\Phi(t)$.

If the stationary state is oscillating harmonically with angular frequency ω, δP_0 may denote the amplitude of the variations of the stationary state value $\bar{P}$. The amplitude δP of the actual fluctuations of P is represented here by a respective relaxation function $\varphi(\omega)$ according to the relation

$$\delta P = \varphi(\omega) \cdot \delta P_0. \qquad (26b)$$

Taking into account Eqs. (22), (23), and (25), the functions $\Phi(t)$ and $\varphi(\omega)$ may be expressed as

$$\Phi(t) = \sum_r \beta_r \cdot \exp(-t/\tau_r),$$
$$\varphi(\omega) = \sum_r [\beta_r/(1+i\omega\tau_r)], \qquad (27)$$

where

$$\beta_r = (\mathring{\alpha}_r/\delta P_0)(\partial P/\partial \alpha_r)_{\alpha_i=0}$$

$$= (\mathbf{y}_r{}^{\dagger}\mathring{\boldsymbol{\gamma}}/\delta P_0)\sum_j (\partial P/\partial \gamma_j)_{\gamma_i=0}\cdot x_{rj} \qquad (28a)$$

and

$$\delta P_0 = \sum_r \mathring{\alpha}_r(\partial P/\partial \alpha_r)_{\alpha_i=0}$$

$$= \sum_r \sum_j (\mathbf{y}_r{}^{\dagger}\mathring{\boldsymbol{\gamma}})(\partial P/\partial \gamma_j)_{\gamma_i=0}\cdot x_{rj}. \qquad (28b)$$

[$x_{rj} = \partial \gamma_j/\partial \alpha_r$ is the jth component of the eigenvector $\mathbf{x}_r$, cf. Eq. (13a).] The obvious relation $\sum_r \beta_r = 1$ reflects the fact that $\Phi(t)$ and $\varphi(\omega)$ become equal to unity for $t \rightarrow 0$ or $\omega \rightarrow 0$, respectively.

In the special, but important, case of relaxation towards chemical equilibrium, the relaxation function $\Phi(t)$ does not involve complex exponential terms. As pointed out above, then $\lambda_r = -1/\tau_r$ can be shown to be an eigenvalue of a symmetric matrix $\mathbf{A}'$ and consequently a real quantity. Thus we may conclude: In any reaction system which is either sufficiently close to its equilibrium or involves reactions of the first order only, periodic reactions (described by complex exponential functions) cannot occur if the temporary equilibrium is changing nonperiodically. Then the relaxation function $\Phi(t)$ may have only m^*-1 maxima or minima, where m^* equals the number of finite relaxation times.[12] This is a consequence of the principle of detailed balance, which ensures the symmetry of $\mathbf{A}'$ [Eqs. (4a), (5b, d)][1,8,12,13]. Far from chemical equilibrium, where this principle does not apply, periodic reactions cannot generally be excluded in agreement with actual experimental observations.[14]

The relaxation function $\varphi(\omega)$ has been defined as a complex quantity. Its absolute amount describes the damping of the (real) amplitude of the oscillations of P, whereas its phase measures the phase shift of δP versus δP_0. We may split $\varphi(\omega)$ into a real and an imaginary part:

$$\varphi(\omega) = \varphi'(\omega) - i\cdot\varphi''(\omega), \qquad (29a)$$

with

$$\varphi'(\omega) = \sum_r [\beta_r/(1+\omega^2\tau_r{}^2)],$$

$$\varphi''(\omega) = \sum_r \beta_r[\omega\tau_r/(1+\omega^2\tau_r{}^2)]. \qquad (29b)$$

The important, experimentally observable relaxation functions $\Phi(t)$, $\varphi(\omega)$, $\varphi'(\omega)$, and $\varphi''(\omega)$ can be converted into each other by mathematical operations. Differentiation of $\Phi(t)$—as represented in (27)—immediately yields.

$$d\Phi/dt = -\sum_r (\beta_r/\tau_r)\cdot \exp(-t/\tau_r). \qquad (30)$$

After multiplying this by $\exp(-i\omega t)$, we find directly that

$$\varphi(\omega) = -\int_0^\infty (d\Phi/dt)\cdot \exp(-i\omega t)\cdot dt \qquad (31a)$$

$$= 1 - i\omega\int_0^\infty \Phi(t)\cdot \exp(-i\omega t)\cdot dt,$$

i.e., $\varphi(\omega)$ is the Fourier transform of $-d\Phi/dt$, and $i[1-\varphi(\omega)]/\omega$ is that of $\Phi(t)$. The practically significant real and imaginary parts of $\varphi(\omega)$, readily yield by means of real Fourier integrals,

$$\varphi'(\omega) = 1 - \omega\int_0^\infty \Phi(t)\cdot \sin\omega t\cdot dt,$$

$$\varphi''(\omega) = \omega\int_0^\infty \Phi(t)\cdot \cos\omega t\cdot dt. \qquad (31b)$$

For a mutual conversion of $\varphi'(\omega)$ and $\varphi''(\omega)$ we have the general Kronig–Kramers relations[15]

$$\varphi'(\omega) = \frac{2}{\pi}\,\mathrm{C}\!\int_0^\infty \frac{u\varphi''(u)}{u^2-\omega^2}\cdot du,$$

$$\varphi''(\omega) = -\frac{2}{\pi}\,\omega\,\mathrm{C}\!\int_0^\infty \frac{\varphi'(u)}{u^2-\omega^2}\cdot du \qquad (32)$$

which hold for any $\omega > 0$ as may be verified readily from Eqs. (29b). (The symbol $\mathrm{C}\!\int$ indicates a Cauchy principal value with regard to the singular point $u = \omega$.)

Inversion of the Fourier integrals in (31b) results in the expressions

$$\Phi(t) = 1 - \frac{2}{\pi}\int_0^\infty \frac{\varphi'(\omega)}{\omega}\sin\omega t\cdot d\omega,$$

$$= \frac{2}{\pi}\int_0^\infty \frac{\varphi''(\omega)}{\omega}\cos\omega t\cdot d\omega. \qquad (33)$$

They may be used to compute $\Phi(t)$ from either $\varphi'(\omega)$ or $\varphi''(\omega)$.

Relaxation Spectra

The distribution of relaxation times as determined by their weight (or amplitude) factors β_r is called the relaxation spectrum of the reaction system with respect to the observable P. Since the relaxation times are derived from a matrix $\mathbf{A}$, which involves only the elementary rate constants and the concentrations of certain reaction partners, the τ_r represent specific properties of the reaction system. Strictly speaking, they depend also on the thermodynamic conditions of the relaxation process (e.g., whether it is adiabatic or isothermal).[13] However, this effect usually can be neglected for chemical reactions in solution.[1] In contrast to the τ_r, the weight factors β_r are essentially determined by the measured quantity P and the

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[12] W. Jost, Z. Naturforsch. **2a**, 159 (1947).

[13] J. Meixner, Kolloid-Z. **134**, 3 (1953).

[14] B. Hess, K. Brand and K. Pye, Biochem. Biophys. Res. Commun. **23**, 102 (1966).

[15] R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926); H. A. Kramers, Physik. Z. **30**, 522 (1929).

boundary conditions of the relaxation process, as is clearly demonstrated by Eq. (28a).

The relaxation spectrum can be calculated on the basis of a definite reaction mechanism, although this may not be practicable in more complex cases. On the other hand, a direct experimental determination of the spectrum is generally not possible. It is the response of some measurable quantity P to a relaxation experiment which can be measured in terms of a relaxation function [e.g., $\Phi(t)$ or $\varphi(\omega)$]. Thus the question is raised whether the relaxation spectrum can be evaluated from an experimentally obtained relaxation function. For instance, can the β_r and τ_r appearing in Eqs. (27) be computed from the respective functions $\Phi(t)$ or $\varphi(\omega)$? There are, in principle, appropriate mathematical procedures to perform such inversions if the relaxation functions are given as analytical functions, especially in the case of virtually continuous spectra (e.g., the method of Fuoss and Kirkwood[16]). In this latter case $\Phi(t)$, for example, essentially becomes a Laplace integral. Then the spectral distribution function is obtained by an inverse Laplace transformation. Unfortunately the relaxation functions are very insensitive with respect to the underlying relaxation spectra; i.e., minor changes of those functions generally result in considerable effects as far as the spectrum is concerned. This was realized years ago in the investigation of dielectric, mechanical, and other relaxation processes.[17–19] With regard to our problem of the spectral analysis of measured chemical relaxation functions, from these considerations we may conclude: *Although it is generally possible to calculate some distribution of relaxation times which yields a good approximation of the experimental curve, this does not necessarily mean that any physical meaning can be attributed to it.* Due to the restricted measuring accuracy, other distributions which are quite different could produce similarly good approximations. Then the spectrum of physical significance determined by the reaction mechanism cannot be detected. Apparently the necessary accuracy of measuring permitting a useful spectral analysis is often far beyond the limits of experimental techniques. Fundamentally we find ourselves confronted with the general problem of fitting theoretical expressions involving adjustable parameters (the β_r, τ_r in our case) to experimental curves. As is well-known, such a procedure becomes less and less trustworthy as the number of those parameters increases. There are favorable cases where satisfactory determinations of relaxation spectra can be carried out. This is true, for instance, if only a few relaxation times occur, and if these differ from each other by at least one order of magnitude. According to the analytical representation given by Eqs. (27), the relaxation functions are then made up of superimposed, but sufficiently separated, partial relaxation curves, each pertaining to one individual relaxation time only. Under these conditions, the mathematical procedure of calculating the τ_r from the relaxation equations can be performed fairly easily. Fortunately, reaction systems of this kind are frequently encountered in practical work (especially as far as the comparatively simple reactions of inorganic and organic chemistry are concerned).[1] It may be possible to determine even a fairly complicated relaxation spectrum from experimental curves if its general functional type is already known, (e.g., as the result of a pertinent theory,) so that only one or two parameters have to be adjusted. For systems where no such favorable circumstances can be utilized to evaluate the complete relaxation spectrum, a kinetic analysis of experimental relaxation curves can still be carried out in terms of mean relaxation times as is demonstrated in the following.

Mean Relaxation Times

Certain mean relaxation times may be introduced as time constants appropriate for the description of the temporal course of a chemical relaxation process. We define the mean reciprocal relaxation time (harmonic mean) τ^* and the arithmetic mean $\tilde{\tau}$ by the relations

$$1/\tau^*=\sum_r (\beta_r/\tau_r), \qquad \tilde{\tau}=\sum_r \beta_r\tau_r, \tag{34}$$

where the respective β_r values appearing in $\Phi(t)$ or $\varphi(\omega)$ are used as weight factors. Such mean values contain less information than the complete relaxation spectrum; they have, however, the great advantage of being much more easily accessible, experimentally as well as theoretically. This is especially true for τ^*.

The mean relaxation times τ^* and $\tilde{\tau}$ are readily correlated to the corresponding relaxation functions. First we have

$$1/\tau^*=-(d\Phi/dt)_{t=0},$$

$$\tilde{\tau}=\int_0^\infty \Phi(t)\,dt, \tag{35}$$

as follows immediately from (30) for $t=0$ and by integration of $\Phi(t)$ as shown in (27), respectively. With respect to $\varphi(\omega)$ we derive the relations

$$1/\tau^*=\frac{2}{\pi}\int_0^\infty \varphi'(\omega)\cdot d\omega=\lim_{\omega\to\infty}\omega\varphi''(\omega), \tag{36a}$$

$$\tilde{\tau}=\frac{2}{\pi}\int_0^\infty \frac{1-\varphi'(\omega)}{\omega^2}\cdot d\omega=\lim_{\omega\to 0}\frac{\varphi''(\omega)}{\omega}, \tag{36b}$$

which can be verified directly by inserting the definitions of $\varphi'(\omega)$ and $\varphi''(\omega)$ according to Eqs. (29b). The experimental significance of the above expressions is discussed in the next section.

The first relation in (35) permits a comparatively

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[16] R. Fuoss and I. G. Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).

[17] F. H. Müller, Kolloid-Z. **134**, 77 (1953).

[18] A. J. Stavermann, Kolloid-Z. **134**, 189 (1953).

[19] E. Hiedemann and R. D. Spence, Z. Physik. **133**, 109 (1952).

simple theoretical access to the mean relaxation time τ^*. A chemical relaxation process is usually initiated by perturbing an originally existing stationary state (for the most part, chemical equilibrium). On the basis of a definite reaction mechanism, the initial relaxation rate due to a stepwise perturbation, and consequently also τ^*, may be then calculated using only elementary rate constants and stationary state (equilibrium) properties of the system. The procedure is demonstrated in more detail in Sec. V. Solving the rate equations, computing the relaxation spectrum, and calculating τ^* according to its definition in (34) would require considerably more effort.

The value of either τ^* or $\tilde{\tau}$ yields no information about the extent of the relaxation spectrum. Only a comparison of both quantities could be utilized for this purpose. A more appropriate way to estimate the width of the spectrum may be obtained by comparing τ^* with the quadratic mean of the $1/\tau_r$:

$$\sum_r (\beta_r/\tau_r^2) = (1/\tau^{**})^2. \tag{37}$$

As can be verified using the representations in (27) and (29b), we have

$$\begin{aligned}(1/\tau^{**})^2 &= (d^2\Phi/dt^2)_{t=0},\\ &= \lim_{\omega\to 0} \omega^2\varphi'(\omega),\\ &= \frac{2}{\pi}\int_0^\infty \{(1/\tau^*) - \omega\varphi''(\omega)\}d\omega.\end{aligned} \tag{38}$$

Apparently τ^{**} is essentially determined by the initial curvature of $\Phi(t)$. Thus it may be computed in an analogous way as pointed out for τ^*. The relative quadratic deviation of $1/\tau_r$ from $1/\tau^*$, i.e.,

$$\begin{aligned}\rho^* &= \frac{\sum_r \beta_r(1/\tau_r - 1/\tau^*)^2}{(1/\tau^*)^2}\\ &= (\tau^*/\tau^{**})^2 - 1,\end{aligned} \tag{39}$$

may be introduced as a measure of the width of the relaxation spectrum, at least for processes with $\beta_r \geq 0$. The latter seems to hold true in many cases of practical interest. It can be shown, for instance, that, sufficiently close to chemical equilibrium the relaxation of certain thermodynamic properties is described by nonnegative β_r values only. (Cf. the case of chemically induced acoustical relaxation discussed in the next section.) In principle, however, negative weight factors, and even negative ρ^* values, cannot be excluded.

A more adequate interpretation of ρ^* can be deduced by expanding the deviation of $\Phi(t)$ from $\exp(-t/\tau^*)$ in a Taylor series. The result may be written as

$$\Phi(t) = \exp(-t/\tau^*) + \tfrac{1}{2}\rho^*(t/\tau^*)^2 + \cdots . \tag{40}$$

Thus ρ^* measures how well $\Phi(t)$ can be approximated by $\exp(-t/\tau^*)$. The sign of ρ^* indicates whether the relaxation proceeds slower ($\rho^* > 0$) or faster ($\rho^* < 0$) than the single exponential function which would occur in case of a one-step process.

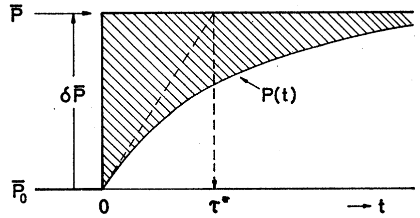

FIG. 1. Chemical relaxation of a measurable quantity P due to stepwise perturbation of a stationary state. The stationary state value $\bar{P}_0$ is suddenly changed to $\bar{P} = \bar{P}_0 + \delta\bar{P}$ at the time $t = 0$. The actual course of $P(t)$ is determined by the kinetics of the system. τ^* is the mean (reciprocal) relaxation time defined by (34).

IV. THE EVALUATION OF RELAXATION EXPERIMENTS

Relaxation Methods Employing Stepwise Perturbation

A sudden perturbation of an existing stationary state (usually the chemical equilibrium) may be executed in some way by rapidly changing the external conditions, thus establishing a different stationary state of the system. Provided the initiated equilibration process can be registered somehow, such a procedure constitutes a very direct mode of measuring chemical relaxation. Pertinent techniques of this kind—especially those producing temperature or pressure jumps[1,20]—have proven to be of considerable versatility and have been applied already to numerous kinetic investigations. Usually, optical density or electric conductivity has served as the measured quantity P.

Let us assume the perturbation takes place at the time $t = 0$, changing the stationary state value of P from $\bar{P}_0$ to $\bar{P} = \bar{P}_0 + \delta\bar{P}$. According to (26a), the time course of P is then described by

$$P = \bar{P} - \Phi(t)\cdot\delta\bar{P}. \tag{41}$$

Thus jump techniques lead directly to the corresponding relaxation function $\Phi(t)$. Furthermore, taking advantage of (35), we immediately find

$$\begin{aligned}(1/\tau^*) &= (1/\delta\bar{P})(dP/dt)_{t=0},\\ \tilde{\tau} &= (1/\delta\bar{P})\int_0^\infty (\bar{P} - P)dt.\end{aligned} \tag{42}$$

One realizes readily how the mean relaxation times τ^* and $\tilde{\tau}$ can be determined graphically from an experimental curve. An example of such a curve is shown in Fig. 1. It is easily verified that the tangent to this curve at the time of perturbation ($t = 0$) intersects the asymptote of the curve at $t = \tau^*$, as demonstrated in the

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[20] G. Czerlinski, *Chemical Relaxation* (M. Dekker, Inc., New York, 1966).

diagram. On the other hand, $\tilde{\tau}$ is apparently given by the area between the curve and its asymptote (dashed area in Fig. 1) divided by $\delta\bar{P}$.

According to (37), (39), and (41), the square mean of the reciprocal relaxation times may be written as

$$(1/\tau^{**})^2 = -(1/\delta\bar{P})(d^2P/dt^2)_{t=0} \\ = [(\rho^*+1)/\tau^{*2}]. \qquad (43)$$

The latter relation can be utilized for a determination of τ^{**} from experimental values of ρ^* and τ^*. The quantity ρ^* is obtained in the following way. First the difference $D(t)=\Phi(t)-\exp(-t/\tau^*)$ has to be evaluated from the relaxation curve. This is suitably done by using a semilogarithmic plot because $\exp(-t/\tau^*)$ is readily drawn then as a straight line which is the tangent to the experimental curve at $t=0$. As shown by Eq. (40), a plot of $2\tau^{*2}\,D(t)/t^2$ versus t finally yields ρ^* by extrapolation towards $t=0$. Apparently, however, the determination of τ^{**} requires a higher measuring accuracy than does the determination of τ^*.

Ultrasonic Relaxation Due to Chemical Relaxation

Periodic perturbations of a chemical equilibrium may be caused by the periodic change of pressure taking place due to the application of a sound wave. Because of the finite relaxation times of the system, the induced changes of concentrations cannot follow the equilibrium fluctuations of the system fast enough if the frequency is sufficiently high. This results in a dispersion of the sound velocity as well as in sound absorption, both of which may be measured and evaluated in terms of the chemical relaxation spectrum. Ultrasonic absorption techniques have already proven very useful in the investigation of many fast reactions in solution, especially in the case of processes which are too fast to be measured by other means.

A sound wave propagating in the x direction induces small oscillations of quantities such as pressure or density to be represented by the expression

$$A\exp\{i\omega[t-(x/v)]\},$$

where

$$v=[(\rho_0\kappa_s)^{-1/2}] \qquad (44)$$

(A = amplitude, ω = angular frequency). The sound velocity v depends on the density ρ_0 and on the adiabatic compressibility

$$\kappa_s = -V^{-1}(\partial V/\partial p)_S \\ = -V^{-1}(\partial V/\partial p)_{S,\alpha_i} \\ -V^{-1}\sum_r(\partial V/\partial\alpha_r)_{S,p,\alpha_i(\neq r)}(\partial\alpha_r/\partial p)_S \qquad (45)$$

(V = volume, p = pressure, S = entropy). The first term represents the adiabatic compressibility of the system without the contribution of the chemical reaction (α_i = const., the α_i being the normal variables); it is to be denoted by κ_s^{∞}. (Frequency dispersion of this term may be neglected in the frequency range of interest for chemical relaxation.) The second term describes the chemical contribution κ_s^{ch}. According to the general definition given in Eq. (26b), it can be written as a product of its equilibrium value $\bar{\kappa}_s^{\mathrm{ch}}$ and the pertinent relaxation function $\varphi(\omega)$:

$$\kappa_s^{\mathrm{ch}} = \bar{\kappa}_s^{\mathrm{ch}}\cdot\varphi(\omega); \qquad \varphi(\omega)=\sum_r[\beta_r/(1+i\omega\tau_r)], \qquad (46a)$$

where

$$\bar{\kappa}_s^{\mathrm{ch}} = -V^{-1}\sum_i b_i; \qquad \beta_r = b_r/\sum_i b_i,$$

$$b_r=(\partial V/\partial\alpha_r)_{S,p,\alpha_i(\neq r)}\cdot(\partial\bar{\alpha}_r/\partial p)_S \qquad (46b)$$

($\bar{\alpha}_r$ is the equilibrium value of α_r). As pointed out by Meixner,[13] $b_r\leq 0$. Consequently, any nonvanishing weight factor β_r describing ultrasonic relaxation close to equilibrium must be a positive quantity.

Now, if we insert $\kappa_s=\kappa_s^{\infty}+\bar{\kappa}_s^{\mathrm{ch}}\cdot\varphi(\omega)$ into (44) while taking into account $\bar{\kappa}_s^{\mathrm{ch}}\ll\kappa_s^{\infty}$, we find the sound wave to be represented by

$$A\cdot\exp(-\alpha x)\cdot\exp\{i\omega[t-(x/v')]\}, \qquad (47a)$$

with

$$v'=v_{\infty}-\Delta v_0\cdot\varphi'(\omega), \qquad \alpha=(\Delta v_0/v_{\infty}^2)\omega\varphi''(\omega), \qquad (47b)$$

where

$$v_{\infty}=(\rho_0\kappa_s^{\infty})^{-1/2}, \\ \Delta v_0=v_{\infty}-v_0=\tfrac{1}{2}\rho_0 v_{\infty}^3\bar{\kappa}_s^{\mathrm{ch}}. \qquad (47c)$$

(v_{∞}, v_0 are limiting values of the sound velocity for very high and very low frequencies, respectively; Δv_0 is the total velocity increment due to chemical relaxation.) Thus the dispersion of the (real) sound velocity v' is described by $\varphi'(\omega)$, while $\varphi''(\omega)$ determines α, the corresponding absorption coefficient of the sound amplitude. Accordingly those relaxation functions can be obtained by appropriate ultrasonic relaxation measurements. Absorption data are frequently evaluated by plotting the absorption coefficient per wavelength $\alpha\lambda$ versus frequency. Apparently this quantity is simply proportional to $\varphi''(\omega)$:

$$\alpha\lambda=2\pi(\Delta v_0/v_{\infty})\varphi''(\omega). \qquad (47d)$$

Also the mean relaxation times τ^* and $\tilde{\tau}$ can be determined directly from the experimental curves. Using (36a, b) and (47b), we get from the velocity dispersion curves by integration,

$$\frac{1}{\tau^*}=\frac{2}{\pi\Delta v_0}\int_0^{\infty}(v_{\infty}-v')\,d\omega,$$

$$\tilde{\tau}=\frac{2}{\pi\Delta v_0}\int_0^{\infty}(v'-v_0)\frac{d\omega}{\omega^2}, \qquad (48a)$$

while they may be obtained from absorption measurements by using limiting values:

$$\tau^*=\Delta v_0/v_{\infty}^2\alpha_{\infty}, \qquad \tilde{\tau}=(v_{\infty}^2/\Delta v_0)(\alpha/\omega^2)_{\omega\to 0}, \qquad (48b)$$

with α_∞ being the total increment of the absorption coefficient (for $\omega \rightarrow \infty$) which is due to chemical relaxation. An advantageous graphical procedure to evaluate τ^* and $\tilde{\tau}$ from absorption curves may be discussed in more detail.

The method is simple if applied to curves described by a single relaxation time τ_r. Such curves are found in cases where there is either only one relaxation time or where the other relaxation times are sufficiently different from τ_r so that their contributions can be neglected in the frequency range around $\omega\tau_r \approx 1$. Then the respective part of α reads

$$\frac{(2\pi\Delta v_0/v_\infty)\beta_r\omega\tau_r}{(1+\omega^2\tau_r^2)}.$$

Any such curve has the same shape if plotted versus frequency on double-logarithmic graph paper. Two examples are given by the dashed curves in Fig. 2. A stencil of the particular curve shape in consideration [described by $x/(1+x^2)$, x being the abscissa] may be adjusted to an experimental curve in order to evaluate its parameters from the coordinates of the vertex $\{[\alpha\lambda]_{\max} = (\pi\Delta v_0/v_\infty)\beta_r,\ \omega_{\max} = 1/\tau_r\}$.

A more complicated situtation is encountered if contributions of more than one relaxation time overlap so much that they cannot be separated clearly. In any case the resulting $\alpha\lambda$ curve—being a superposition of the simple functions $\omega\tau_r/(1+\omega^2\tau_r^2)$ multiplied by a weight factor—is broader and flatter than the curve type described by a single relaxation time. This is the obvious consequence of the fact that the β_r must be positive. The solid curve in Fig. 2 illustrates an example of such a composite $\alpha\lambda$ curve.

According to (47d) and (36a), we find

$$\alpha\lambda \rightarrow 2\pi(\Delta v_0/v_\infty)/\omega\tau^*$$

for $\omega \rightarrow \infty$. The same holds true for the auxiliary curve

$$(2\pi\Delta v_0/v_\infty\omega\tau^*/(1+\omega^2\tau^{*2}),$$

which is easily drawn using the stencil mentioned above. One has to adjust its high-frequency part to that of the experimental curve while placing its vertex at an ordinate value of $\pi\Delta v_0/v_\infty$ (which must be known from experiments or by calculations). Then the vertex will appear at $\omega = 1/\tau^*$. This graphical procedure is demonstrated in Fig. 2. It is, of course, equivalent to the analytical relation in (48b). If the stencil is adjusted to the low-frequency part of the $\alpha\lambda$ curve, the same method yields $\tilde{\tau}$ as also can be seen in Fig. 2. This is a consequence of

$$\alpha\lambda \rightarrow 2\pi(\Delta v_0/v_\infty)\omega\tilde{\tau}$$

for $\omega \rightarrow 0$, which results from (47d) and (36b) or (48b), respectively.

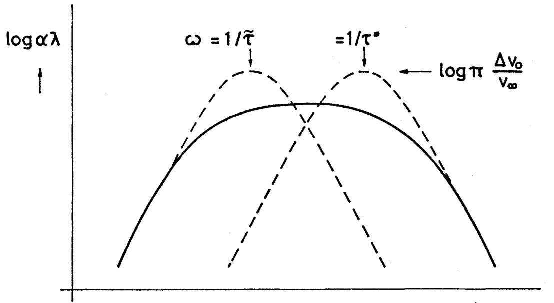

FIG. 2. Double logarithmic plot of the sound absorption coefficient per wavelength $\alpha\lambda$ versus frequency f ($\omega = 2\pi f$). The dashed curves correspond to $\alpha\lambda(\omega)$ plots for a one-step process (with a single relaxation time). They may be drawn by means of a stencil and used as auxiliary curves for the determination of $\tilde{\tau}$ and τ^* as pointed out in the text.

Other Relaxation Methods Employing Periodic Perturbations

In principle, any relaxation process involving periodic perturbations of angular frequency ω yields the relaxation function $\varphi(\omega)$ of the respective measured quantity and may be treated analogously to the ultrasonic case. So far, however, there is only one more such process which is of certain significance for chemical relaxation measurements, i.e., dielectric relaxation. It has been shown theoretically as well as experimentally that reactions taking place in a strong static electric field may display dielectric dispersion due to perturbations by a small superimposed periodic electric field.[21] Actually such an effect may be found even without applying the static field if chemical relaxation proceeds faster than orientational relaxation.[22] This can be expected, e.g., for conformational changes of biopolymers.[23]

V. DETERMINATION OF RATE AND MECHANISM OF A REACTION BY MEANS OF RELAXATION DATA

Fundamental Aspects

In principle, chemical relaxation methods may be applied to reaction systems of any complexity. Of course, useful results can be expected only under conditions yielding sufficient perturbation and measurable response of the special system under consideration. Then a relaxation function and certain mean relaxation times may be determined directly from the experimental data as pointed out above. The minimum number of discrete individual relaxation times which can be recognized from the shape of the measured curve indicates a minimum number of elementary processes involved in the over-all reaction. A more detailed evaluation of the relaxation experiment with regard to rate and mechanism usually requires more information about the system—such as the results of

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[21] K. Bergmann, M. Eigen, and L. de Maeyer, Ber. Bunsenges. Physik. Chem. 67, 819 (1963).

[22] G. Schwarz, J. Phys. Chem. (to be published).

[23] G. Schwarz, in *Molecular Relaxation Processes* (The Chemical Society, London 1966), Special Publication No. 20, p. 191.

more relaxation experiments under different conditions, as well as thermodynamic data. A few reasonable hypothetical reaction mechanisms can then be tested by comparing their theoretically calculated relaxation behavior with the experimental findings. If there is no agreement, the mechanism being considered is incorrect and can be ruled out. Once sufficient evidence has been found to indicate that a certain mechanism is the true one, the theoretical relations between the rate constants and the experimentally accessible individual or mean relaxation times may be calculated and utilized to determine those rate constants.

Discrete Relaxation Spectra

A spectrum of relaxation times which are sufficiently different from each other to be distinctly recognized in the over-all relaxation curve is called a discrete relaxation spectrum. Spectra of this kind are encountered in the case of fairly uncomplicated reaction mechanisms comprising only a few elementary processes which differ considerably in their respective rates. Then the individual relaxation times may be calculated without serious difficulties following the procedure pointed out above. The analysis of such reactions—in particular, processes characterized by only one relaxation time (i.e., one-step reactions)—has been discussed in detail elsewhere.[1]

Due to degeneracy phenomena, even rather complicated reaction systems may display a relatively simple discrete relaxation spectrum. This is shown, for instance, by the recently elucidated allosteric binding mechanism of the enzyme glycerol-aldehyde-3-phosphate dehydrogenase (from yeast) and nicotinamide-adenine-dinucleotide (NAD).[24] In spite of the presence of nine linearly independent elementary processes here only three relaxation times actually occur. That could be clearly recognized from the relaxation curves. The investigation of this system represents an excellent example of the exceedingly valuable potentialities offered by chemical relaxation methods for the study of a fairly complex reaction.

Complex Relaxation Spectra

As has been emphasized already, individual relaxation times may differ too little to be determined accurately enough from the measured relaxation functions. Under unfavorable conditions this may happen even for a two-step process. Naturally, such complex relaxations can be expected to a greater extent in systems with a large number of relaxation times (i.e., with a large number of intermediate reaction steps). Since, under these conditions, the mean relaxation times τ^* and $\tilde{\tau}$ can still be determined from the experimental curves, a kinetic ananlysis can be attempted in terms of these quantities. Unfortunately, however, the solution of the complete relaxation problem is frequently not practicable for complex systems described by too many relaxation times, as has also been emphasized before. In such cases τ^* and $\tilde{\tau}$ cannot be calculated according to Eqs. (34). Under these circumstances it becomes especially advantageous to use τ^* because it can be calculated without a complete solution of the relaxation equations, no matter how complicated they are.

Calculation and Significance of τ^* for a General Reaction System

We consider the general system introduced in Sec. II. According to (2), the net rate of the sth elementary process reads

$$v_s - v_s' = k_s' \{ K_s c_1^{\nu_{s1}} c_2^{\nu_{s2}} \cdots c_m^{\nu_{sm}} - c_1^{\nu'_{s1}} c_2^{\nu'_{s2}} \cdots c_m^{\nu'_{sm}} \}. \tag{49a}$$

This equals zero if we assume chemical equilibrium to be established ($c_i = \bar{c}_i$). A sudden change of the equilibrium conditions at $t=0$ (e.g., by a temperature jump) resulting in $k_s' \to k_s' + \delta k_s'$, $K_s \to K_s + \delta K_s$ then yields an initial net rate of

$$(v_s - v_s')_{t=0} = (k_s' + \delta k_s') \cdot \bar{c}_1^{\nu_{s1}} \bar{c}_2^{\nu_{s2}} \cdots \bar{c}_m^{\nu_{sm}} \cdot \delta K_s \tag{49b}$$

In case of a small perturbation of equilibrium, $\delta k_s'$ may be neglected. Now utilizing (42) and (3), a relation for the mean relaxation time τ^* pertaining to the measurable quantity P can be derived:

$$\begin{aligned} 1/\tau^* &= (\delta \bar{P})^{-1} (dP/dt)_{t=0} \\ &= (\delta \bar{P})^{-1} \sum_i (\partial P/\partial c_i)_{c_i = \bar{c}_i} (dc_i/dt)_{t=0} \\ &= \sum_s g_s k_s, \end{aligned} \tag{50a}$$

where

$$g_s = \bar{c}_1^{\nu_{s1}} \bar{c}_2^{\nu_{s2}} \cdots \bar{c}_m^{\nu_{sm}} (\delta \ln K_s / \delta \bar{P}) \times \sum_i (\nu_{si} - \nu_{si}') (\partial P / \partial c_i)_{c_i = \bar{c}_i} \tag{50b}$$

is determined by equilibrium properties of the system ($\delta \ln K_s$, $\delta \bar{P}$ = total changes of $\ln K_s$, and $\bar{P}$ due to the change of equilibrium). In an analogous way, τ^* may be obtained for small perturbations of other stationary states.

The above procedure remains useful even for a large perturbation described by $K_s^0 \to K_s^\infty$, $k_s^0 \to k_s^\infty$, $\bar{c}_{i0} \to \bar{c}_{i\infty}$. Evidently the initial slope of the P curve can be calculated according to (50a, b), with $k_s = k_s^\infty$ and $\bar{c}_i = \bar{c}_{i0}$, while $\delta \ln K_s / \delta \bar{P}$ has been substituted for by

$$(\Delta K_s / \Delta \bar{P}) / K_s^\infty \quad (\Delta K_s = K_s^\infty - K_s^0,\ \Delta \bar{P} = \bar{P}^\infty - \bar{P}^0).$$

One has to bear in mind, however, that under these circumstances τ^* can be interpreted as a mean relax-

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[24] K. Kirschner, M. Eigen, R. Bittman, and B. Voigt, Proc. Natl. Acad. Sci. (U.S.) **56**, 1661 (1966).

ation time only if all the elementary reactions are of the first order; otherwise it has only formal meaning.

Since τ^* depends on P, on the $\bar{c}_i$, and on the expression $\delta \ln K_s/\delta \bar{P}$, (which is determined by the special kind of relaxation experiment under consideration,) variation of these quantities may permit one to measure many different relaxation times τ^*_j $(j=1, 2, \cdots, N)$ with the same system. On the basis of a given reaction mechanism, the above theory yields the equations

$$1/\tau_j^* = \sum_s g_{js}k_s \qquad (j=1, 2, \cdots, N), \tag{51}$$

involving pertinent thermodynamic coefficients g_{js}. Comparison of these relations with experimental data offers valuable assistance in searching for the true reaction mechanism. If that mechanism is known, Eq. (51) may be utilized to determine rate constants from the measured τ^* values. Two definite cases of practical interest may be considered to demonstrate the virtues of the procedure.

Example I: Cooperative Intramolecular Transformations of Biopolymers[5]

Such processes proceed via a huge number of intermediate reaction steps. Consequently they are characterized by a virtually continuous relaxation spectrum. Since its evaluation encounters considerable difficulties, an analysis in terms of τ^* is suitable here. A detailed discussion for the special case of the helix-coil transition of polypeptides can be found elsewhere.[3,4] An investigation of the general problem [5,6] is in progress.

Example II: An Allosteric System

Another important reaction scheme of biological significance is the allosteric binding mechanism proposed by Monod *et al.*[25] A substance E (e.g., an enzyme) may exist in two states, T_0 and R_0, each of which has n identical binding sites for the ligand F. The affinity of binding is assumed to be different for the T and the R states. For the sake of simplicity we consider here merely the special case with no binding to the T state. If R_i means that i sites of R are occupied by the ligand, the complete reaction system can be formulated by means of the following $n+1$ elementary processes:

$$T_0 \underset{k'}{\overset{k}{\rightleftharpoons}} R_0; \qquad R_{i-1}+F \underset{ik_D}{\overset{(n-i+1)k_R}{\rightleftharpoons}} R_i \qquad (i=1, 2, \cdots n,). \tag{52}$$

Recombination and dissociation of a single binding site and a ligand molecule are described by the rate constants k_R and k_D, resepectively. $K_A = k_R/k_D$ is to be called the "microscopic" association constant, $L = k'/k$ the "allosteric" constant. The various symbols, E, T_0, and R_i, may be used also to denote the corresponding concentrations. Then $B = \sum_i iR_i$ equals the concentration of occupied binding sites (bound ligands). With S, F, and F_{tot} being the concentrations of free sites, free ligand, and total ligand, respectively, we have

$$B+S+nT_0 = nE; \qquad B+F = F_{\text{tot}}, \tag{53}$$

where the first relation describes the conservation of binding sites, while the second one is due to the conservation of the ligand.

That fraction of the maximum concentration of binding sites which is actually occupied, i.e., $Y = B/(nE)$, may be called the degree of saturation. It is usually a measurable quantity. On the basis of (52) and (53), the equilibrium values of Y and T_0 can be readily evaluated to be

$$\bar{Y} = a(1+a)^{n-1}/[L+(1+a)^n],$$
$$\bar{T}_0 = \{L/[L+(1+a)^n]\}\cdot E. \tag{54}$$

A plot of $\bar{Y}$ versus $a = K_A\bar{F}$ yields a sigmoidal curve of the type encountered with allosteric systems. K_A and L can be determined by adjusting the theoretical curves to the experimental ones.

The reactions (52) are described by $n+1$ linearly independent rate equations. Thus, in general, the relaxation spectrum of the system is composed of $(n+1)$ individual relaxation times. Let us consider only the two equations describing the temporal change of the occupied sites and that of T_0, respectively:

$$dB/dt = k_RF\cdot S - k_DB = k_D\{K_ASF - B\}, \tag{55a}$$
$$dT_0/dt = k'R_0 - kT_0 = k\{LR_0 - T_0\}. \tag{55b}$$

If the unimolecular transition $T_0 \leftrightarrow R_0$ is frozen, the identical binding sites on the various R states do not differ from each other. Then the n binding processes of (52) degenerate into one process, namely the recombination–dissociation process of the ligand and the binding sites as represented by (55a). Only the relaxation time τ_B for this one-step process will occur so far as the relaxation of Y or F is concerned. The contributions of the other $(n-1)$ relaxation times formally associated with the system vanish because of zero weight factors (cf., Kirschner *et al.*[24]). The situation remains essentially the same so long as the transition $T_0 \leftrightarrow R_0$ proceeds much more slowly than the binding. This process, however, contributes a second relaxation time τ_T. It can be calculated from (55b) under the assumption that R_0 is always in equilibrium with the other R_i. We find readily from (55a, b) that

$$1/\tau_B = k_R(\bar{S}+\bar{F}) + k_D,$$
$$1/\tau_T = k + [k'/(1+a)^n], \tag{56}$$

with $\tau_B \ll \tau_T$.

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[25] J. Monod, J. Wyman, and J.-P. Changeux, J. Mol. Biol. **12**, 88 (1965).

If the allosteric conversion $T_0 \leftrightarrow R_0$ is not sufficiently slow, it changes R_0 during the relaxation of Y (or F). Due to this effect, the binding sites on the various R_i species become distinguishable from each other; consequently the relaxation spectrum is no longer degenerate. In general, all the $(n+1)$ relaxation times now appear. The resulting complex spectrum is suitably evaluated using mean relaxation times. Let us assume that Y and T_0 can be measured. Step-wise perturbation of an original equilibrium (at $t=0$) described by $K_A \rightarrow K_A+\delta K_A$, $L \rightarrow L+\delta L$ yields, according to (55a, b):

$$\begin{aligned}(dB/dt)_{t=0}&=k_D\cdot\bar{S}\cdot\bar{F}\cdot\delta K_A,\\ (dT_0/dt)_{t=0}&=k\cdot\bar{R}_0\cdot\delta L.\end{aligned}\tag{57}$$

According to (42), this may be transformed to the relations

$$\begin{aligned}(\tau_Y{}^*)^{-1}&=(\delta\bar{Y})^{-1}(dY/dt)_{t=0}\\ &=k_D(\delta\ln K_A/\delta\ln\bar{Y}),\\ (\tau^*{}_T)^{-1}&=(\delta\bar{T}_0)^{-1}(dT_0/dt)_{t=0}\\ &=k(\delta\ln L/\delta\ln\bar{T}_0).\end{aligned}\tag{58}$$

correlating the rate constants k_D and k with the mean reciprocal relaxation times pertaining to $Y(=B/(nE))$ and T_0, respectively. The thermodynamic factors may be calculated by means of (54); they may also be determined experimentally from equilibrium properties of the system. In the case of perturbation by a temperature jump, we have

$$\begin{aligned}\frac{\delta\ln K_A}{\delta\ln\bar{Y}}&=\frac{(\Delta H_A/RT^2)}{d\bar{Y}/dT}\bar{Y},\\ \frac{\delta\ln L}{\delta\ln\bar{T}_0}&=\frac{(\Delta H_L/RT^2)}{d\bar{T}_0/dT}\bar{T}_0.\end{aligned}\tag{59}$$

(T is the absolute temperature, ΔH_A and ΔH_L are the molar enthalpy changes of the "microscopic" association and the "allosteric" conversion, respectively.)

While it should usually be possible to measure Y, there might be no experimental access to T_0. Then, of course, k (or k') cannot be obtained from τ^* measurements. It may be evaluated, however, from the $\tilde{\tau}$ value or the course of the relaxation curve, provided that $\tilde{\tau}$ or the relaxation function can be calculated—possibly by means of a computer. If k_R (or k_D) and the pertinent thermodynamic properties are known, k (or k') is the only unknown quantity to be determined by comparing the experimental and theoretical results. In case the calculations are too tedious to be carried out, there is still the possibility of determining $\tau_T{}^*$ via the square mean of the reciprocal relaxation times. How this latter quantity can be determined experimentally has been pointed out in Sec. IV. Its theoretical calculation does not require a complete solution of the relaxation problem. The differentiating of (55a) and the taking into account of (53) yields

$$\begin{aligned}(d^2B/dt^2)_{t=0}=-[k_R(\bar{S}+\bar{F})+k_D](dB/dt)_{t=0}&\\ -nk_R\bar{F}(dT_0/dt)_{t=0}.&\end{aligned}\tag{60a}$$

After expressing B by Y, further transformations using (43), (56), (58), and (54) finally lead to

$$\left(\frac{1}{\tau_Y{}^{**}}\right)^2=\frac{1}{\tau_Y{}^*}\left[\frac{1}{\tau_B{}^*}+\frac{L}{(1+a)^{n-1}}\cdot\frac{1}{\tau_T{}^*}\right].\tag{60b}$$

This relation permits the determination of $\tau_T{}^*$ from $\tau_Y{}^{**}$ by means of equilibrium parameters only, provided that $\tau_Y{}^*$ is already known.

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