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THE INTERPRETATION OF
ULTRASONIC RELAXATION SPECTRA
WITHIN THE THEORY OF
IRREVERSIBLE THERMODYNAMICS

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Synopsis

Explicit expressions are given for the ultrasonic absorption spectrum caused by several coupled chemical reactions. The expressions are exact within the theory of irreversible thermodynamics and are given in a form which makes it easy to calculate the relaxation spectrum for a given kinetic model from knowledge of the rate constants and normally used thermodynamic parameters. The article also suggests approximations in terms of one or a few relaxation times of the relaxation spectrum caused by several reactions.

I. Introduction

The interpretation of relaxation experiments within the theory of irreversible thermodynamics in the case of a single chemical degree of freedom has been treated very thoroughly in several places (see e.g. ref 1). When one wants to treat the possibility of more than a single chemical reaction, one normally makes at least one of the following approximations. Either one treats the coupling between the chemical reactions correctly but supposes that the concentrations are small so that the coupling between the chemical degrees of freedom and the physical degrees of freedom (p and T) can be neglected (2). Or one supposes that the relaxation times for the different chemical reactions are separated so much that the coupling between the different chemical reactions can be neglected.

Only in one article (3) does it seem possible to find the correct treatment without other assumptions than the general assumptions of irreversible thermodynamics. This article, however, still leaves several questions open for the experimentalist, who wants to interpret his results in terms of a multi-step mechanism. The most important of these questions are:

1) How are the functions ε and A in the general rate equation of irreversible thermodynamics

$$\frac{d\xi}{dt} = \varepsilon(p, T, \xi) A(p, T, \xi) \quad (1)$$

transformed into normal kinetic parameters?

2) What is the connection between the kinetic and thermodynamic parameters and the weight-factors of the different relaxation times? e.g. the A 's in the expression for the attenuation factor as a function of the frequency ω :

$$\frac{\alpha}{\omega^2} = \sum_{j=1}^n \frac{A_j}{1 + (\omega \tau_j)^2} \quad (2)$$

where the τ 's are the relaxation times

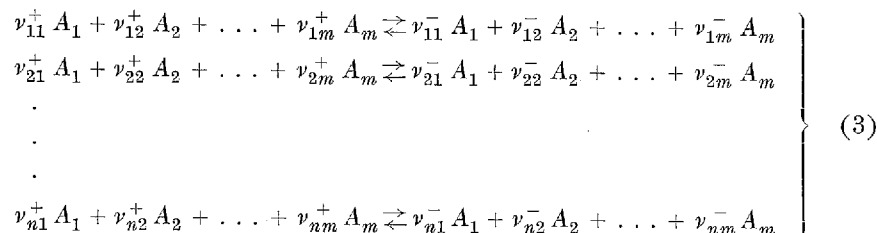
3) If one makes one of the above-mentioned approximations, how large is then the error-term?

4) Is it possible to describe the results from measurements on multistep-mechanisms with one or two relaxation times and how will these parameters then be connected with the kinetic and thermodynamic parameters?

It is the purpose of this article to try to answer these questions. Expressions will be given explicitly for the frequency dependence of the attenuation factor in the case of ultrasonic absorption, but the general approach should equally well be applicable to other types of relaxation measurements. The treatment given here is closely related to that of the Groot and Mazur (1) for a single chemical reaction to which one should refer for a more detailed explanation of the problems of irreversible thermodynamics.

II. The rate equations

The general reaction scheme for n different chemical reactions involving altogether m different chemical species, A_1, A_2, \dots, A_m , may be written:



where many of the coefficients, ν^+ and ν^- , of course, may be zero, since chemical reactions are normally either unimolecular or bimolecular.

The rate equations for the system (3) are most easily stated by first introducing a reaction parameter ξ_i for each of the n reactions ($i = 1, 2, \dots, n$). ξ_i measures the change in chemical composition from the time t_0 until the time t caused by the i 'th reaction, such that the change in the number of moles of A_1 from time t_0 to time t caused by the first reaction will be $(\nu_{11}^- - \nu_{11}^+) \xi_1$, owing to the second reaction the change will be $(\nu_{21}^- - \nu_{21}^+) \xi_2$, and so on. Altogether the change in the number of moles of A_1 from time t_0 to time t_1 will be equal to

$$x_1 = \sum_{i=1}^n (\nu_{i1}^- - \nu_{i1}^+) \xi_i. \quad (4a)$$

Similar for the change in the number of moles of A_2 :

$$x_2 = \sum_{i=1}^n (\nu_{i2}^- - \nu_{i2}^+) \xi_i \quad (4b)$$

etc. for A_3, A_4, \dots, A_m . These and the following equations can be brought into a more convenient form by introducing a matrix notation:

$$\xi^T = \{\xi_1, \xi_2, \dots, \xi_n\}. \quad (5)$$

(All vectors are supposed to be column vectors. Superscript T stands for transposing and consequently ξ^T is a row vector)

$$\mathbf{x}^T = \{x_1, x_2, \dots, x_n\}. \quad (6)$$

$$\mathbf{N} = \begin{Bmatrix} v_{11}, v_{12}, \dots, v_{1m} \\ v_{21}, v_{22}, \dots, v_{2m} \\ \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \\ v_{n1}, v_{n2}, \quad v_{nm} \end{Bmatrix} \quad (7)$$

$$v_{ij} = v_{ij}^- - v_{ij}^+. \quad (8)$$

With this notation the equations (4) read:

$$\mathbf{x} = \mathbf{N}^T \xi. \quad (9)$$

Note that knowledge of a given chemical composition at time t_0 and a given chemical composition at time t are not always sufficient information to determine the ξ_i 's uniquely. The composition at time t_0 together with the rate equations given below, however are always sufficient to determine the ξ_i 's uniquely.

Using k_i for the forward and k_{-i} for the backward rate constant for the i 'th reaction ($i = 1, 2, \dots, n$), the normal rate equations for the system of chemical reactions (3) are:

$$\left. \begin{aligned} \frac{1}{V} \frac{d\xi_1}{dt} &= k_1 \prod_{j=1}^m c_j^{v_{1j}^+} - k_{-1} \prod_{j=1}^m c_j^{v_{1j}^-} \\ \frac{1}{V} \frac{d\xi_2}{dt} &= k_2 \prod_{j=1}^m c_j^{v_{2j}^+} - k_{-2} \prod_{j=1}^m c_j^{v_{2j}^-} \\ &\cdot \\ &\cdot \\ &\cdot \\ \frac{1}{V} \frac{d\xi_n}{dt} &= k_n \prod_{j=1}^m c_j^{v_{nj}^+} - k_{-n} \prod_{j=1}^m c_j^{v_{nj}^-} \end{aligned} \right\} \quad (10)$$

where V is the volume and c_j is the concentration in moles/liter of A_j ($j = 1, 2, \dots, m$). As defined by equation (10) the rate constants k_i and k_{-i} will in general depend not only on p and T but also on the concentrations. In order to get through with the calculations one will need some specific assumption about the dependence of the rate constants on the concentrations. It is common to just take the simplest way out and assume that the rate constants are independent of the concentrations. This approximation, however, has some less satisfactory consequences.

Equations (10) implies the equilibrium conditions:

$$0 = \frac{d\xi_i/V}{dt} = k_i \prod_{j=1}^m c_j^{\nu_{ij}^+} - k_{-i} \prod_{j=1}^m c_j^{\nu_{ij}^-} \quad (11)$$

or:

$$\prod_{j=1}^m c_j^{\nu_{ij}} = \frac{k_i}{k_{-i}} = K_i \quad (12)$$

where K_i is the equilibrium constant for the i 'th reaction. Writing μ_j for the chemical potential of the j 'th component and g_i for the molar change in chemical potential due to the i 'th reaction:

$$g_i = \sum_{j=1}^m \nu_{ij} \mu_j \quad (13)$$

eqn (12) implies

$$g_i = g_i^0 + RT \ln \prod_{j=1}^m c_j^{\nu_{ij}} \quad (14)$$

$$g_i^0 = -RT \ln K_i. \quad (15)$$

Since the number of moles can only change by the chemical reactions, the differential of the Gibbs' free energy:

$$dG = -S dT + V dp + \sum_{j=1}^m \mu_j dx_j \quad (16)$$

can be written:

$$dG = -S dT + V dp + \sum_{i=1}^n g_i d\xi_i \quad (17)$$

and one consequently has the following Maxwell relation

$$\left(\frac{\partial g_i}{\partial \xi_k} \right)_{p, T, \xi^-} = \left(\frac{\partial g_k}{\partial \xi_i} \right)_{p, T, \xi^-} \quad (18)$$

where the index ξ^- means that all other ξ 's are kept constant. Using eqn. (14) and the assumption that g_i^0 depends only on p and T , eqn. (18) gives

$$\frac{RT}{V} \Delta v_i \left(\frac{\delta V}{\delta \xi_k} \right)_{p, T, \xi^-} = \frac{RT}{V} \Delta v_k \left(\frac{\delta V}{\delta \xi_i} \right)_{p, T, \xi^-} \quad (19)$$

with

$$\Delta v_i = \sum_{j=1}^m \nu_{ij} \quad (20)$$

The implication of (19), namely that change in volume by the i 'th reaction is proportional to the change in moles (Δv_i) by the i 'th reaction with a proportionality factor, which does not depend on i , is of course fulfilled for the ideal gases, but seems less satisfactory for solutions. (Note that the problem only arises in case of more than one chemical reaction). In many cases it will of course be a reasonable approximation for solutions to put $\left(\frac{\delta V}{\delta \xi_i} \right)_{p, T, \xi^-}$ equal to zero, which solves the problem.

Here, however, we will prefer the more general solution which is obtained by using molar fractions in place of concentrations, and then in the end merely state the results for g_i^0 only depending on p and T . With z_j for the molar fraction of the j 'th component, ν for the total number of moles and tildes on new parameters we get the following equations in place of equations (10), (12), (14) and (15):

$$\frac{d\xi_i}{dt} = \nu \left(\tilde{k}_i \prod_{j=1}^m z_j^{\nu_{ij}^+} - \tilde{k}_{-i} \prod_{j=1}^m z_j^{\nu_{ij}^-} \right) \quad (21)$$

$$\tilde{K}_i = \prod_{j=1}^m z_j^{\nu_{ij}} \quad (22)$$

$$g_i = \tilde{g}_i^0 + RT \ln \prod_{j=1}^m z_j^{\nu_{ij}} \quad (23)$$

$$\tilde{g}_i^0 = -RT \ln \tilde{K}_i \quad (i = 1, 2, 3, \dots, n) \quad (24)$$

where it now is supposed that g_i^0 and k_i and k_{-i} only depend on p and T but are independent of the molar fractions. The rate equation (21) (respectively (10)) is different from the rate equation (1), which is the one normally used in irreversible thermodynamics. If one writes (21) as

$$\frac{d\xi_i}{dt} = \nu \tilde{\gamma}_i^2 (1 - \exp(g_i/RT)) \quad (25)$$

$$\tilde{\gamma}_i^2 = \tilde{k}_i \prod_{j=1}^m z_j^{\nu_{ij}^+} \quad (26)$$

it is easily seen that the two equations become identical when one only keeps terms that are linear in the deviation from equilibrium, which is the normal approximation of irreversible thermodynamics.

Making this approximation one gets the rate equations:

$$\left. \frac{d\xi_i}{dt} = \nu \tilde{\gamma}_i^2 \left[\frac{1}{RT^2} \left(\frac{\delta H}{\delta \xi_i} \right)_{p, T, \xi^-} \delta T - \frac{1}{RT} \left(\frac{\delta V}{\delta \xi_i} \right)_{p, T, \xi^-} \delta p + \frac{1}{\nu} \sum_{k=1}^n \left(\Delta \nu_i \Delta \nu_k - \sum_{j=1}^m \frac{\nu_{ij} \nu_{kj}}{z_j} \right) \xi_k \right] \right\} \quad (27)$$

$$(i = 1, 2, 3, \dots, n).$$

where we have chosen the reference time, t_0 , to correspond to the equilibrium state at the pressure p and the temperature T , so that ξ and \mathbf{x} measure deviations from this equilibrium state, while the deviation on other variables from this reference state is designated by a δ .

In matrix notation the equations (27) read:

$$\dot{\xi} = \tilde{\mathbf{G}}^2 \left[\frac{\nu}{RT^2} \delta T \mathbf{h} - \frac{\nu}{RT} \delta p \mathbf{v} + (\nu \nu^T - \mathbf{N} \mathbf{Z}^{-1} \mathbf{N}^T) \xi \right] \quad (28)$$

where we have introduced the following vectors and matrices:

$$\mathbf{h}^T = \left\{ \left(\frac{\delta H}{\delta \xi_1} \right)_{p, T, \xi^-}, \left(\frac{\delta H}{\delta \xi_2} \right)_{p, T, \xi^-}, \dots, \left(\frac{\delta H}{\delta \xi_n} \right)_{p, T, \xi^-} \right\} \quad (29)$$

$$\mathbf{v}^T = \left\{ \left(\frac{\delta V}{\delta \xi_1} \right)_{p, T, \xi^-}, \left(\frac{\delta V}{\delta \xi_2} \right)_{p, T, \xi^-}, \dots, \left(\frac{\delta V}{\delta \xi_n} \right)_{p, T, \xi^-} \right\} \quad (30)$$

$$\nu^T = \{\Delta \nu_1, \Delta \nu_2, \dots, \Delta \nu_n\} = \mathbf{e}^T \mathbf{N}^T \quad (31)$$

$$\mathbf{e}^T = \{1, 1, 1, \dots, 1\} \quad (32)$$

$$\tilde{\mathbf{G}} = \begin{pmatrix} \tilde{\gamma}_1 & 0 & 0 & \dots & 0 \\ 0 & \tilde{\gamma}_2 & 0 & \dots & 0 \\ 0 & 0 & \tilde{\gamma}_3 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & \tilde{\gamma}_n \end{pmatrix} \quad (33)$$

$$\mathbf{Z} = \begin{pmatrix} z_1 & 0 & 0 & \dots & 0 \\ 0 & z_2 & 0 & \dots & 0 \\ 0 & 0 & z_3 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & z_m \end{pmatrix} \quad (34)$$

In many cases it will be useful to reduce the number of chemical variables to a minimum. This is attained by reducing the number of rows in \mathbf{N} . In general the rows of \mathbf{N} will not be linearly independent, but it can of course always be arranged that the first n' rows are independent and that the remaining $n-n'$ rows can be written as linear combinations of the first n' rows. With \mathbf{N}' for the matrix consisting of the first n' row of \mathbf{N} , this means that

$$\mathbf{N} = \mathbf{B}\mathbf{N}' \quad (35)$$

where \mathbf{B} is $n \times n'$ matrix, whose first n' rows are identical with the $n' \times n'$ identity matrix. According to the definition n' is equal to the rank of \mathbf{N} . Since it follows from the conservation of mass, that there exists at least one linear relation between the columns of \mathbf{N} the following restriction on n' is evident

$$n' \leq m-1. \quad (36)$$

Using \mathbf{y} for the n' -dimensional vector, whose elements are the new, independent chemical variables (9) is changed to:

$$\mathbf{x} = \mathbf{N}'^T \mathbf{y} \quad (37)$$

$$\mathbf{y} = \mathbf{B}^T \xi. \quad (38)$$

Note that \mathbf{y} is not just the first n' elements of ξ . (It is of course possible

to choose other basic sets of variables than \mathbf{y} by substituting $\mathbf{D}^{-1}\mathbf{y}$ for \mathbf{y} , \mathbf{BD} for \mathbf{B} and $\mathbf{D}^{-1}\mathbf{N}'$ for \mathbf{N}' where \mathbf{D} is any non-singular $n' \times n'$ matrix).

The physical interpretation of the reduction from the variables ξ to the variables \mathbf{y} is, that the first n' reactions in (3) are really independent while the remaining reactions can be written as linear combinations of the first n' reactions. This means that if \mathbf{h}' , \mathbf{v}' and \mathbf{v} are n' dimensional vectors whose components are the first n' components of \mathbf{h} , \mathbf{v} , and \mathbf{v} respectively, then one has the relations

$$\mathbf{h} = \mathbf{B}\mathbf{h}' \quad (39)$$

$$\mathbf{v} = \mathbf{B}\mathbf{v}' \quad (40)$$

$$\mathbf{v} = \mathbf{B}\mathbf{v}'. \quad (41)$$

The similar equation for the $g_i^{\tilde{0}}$'s gives that chemical equilibrium is determined by the first n' equations of (22), and that the remaining $n-n'$ equations automatically are fulfilled, if the first n' are fulfilled.

The final form of the rate equation then becomes:

$$\dot{\mathbf{y}} = \tilde{\mathbf{G}}'^2 \left[\frac{\nu}{RT^2} \delta T \mathbf{h}' - \frac{\nu}{RT} \delta p \mathbf{v}' - (\mathbf{N}' \mathbf{Z}^{-1} \mathbf{N}'^T - \nu' \nu'^T) \mathbf{y} \right] \quad (42)$$

with

$$\tilde{\mathbf{G}}'^2 = \mathbf{B}^T \mathbf{G}^2 \mathbf{B}. \quad (43)$$

III. The attenuation factor

In order to find the attenuation factor at the frequency ω one has primarily to find $\frac{\delta p}{\delta V}$ at constant entropy under the assumption that the deviations of the variables vary harmonically with time with the frequency ω . The condition of the entropy being constant is attained by introducing the additional equations

$$\delta S = \frac{\nu C_p}{T} \delta T - V l \delta p + \frac{1}{T} \mathbf{h}'^T \mathbf{y} = 0 \quad (44)$$

where we have used that at equilibrium ($g_i = 0$):

$$\left(\frac{\delta S}{\xi_i} \right)_{p, T, \xi^-} = \frac{1}{T} \left(\frac{\delta H}{\xi_i} \right)_{p, T, \xi^-} \quad (45)$$

Here C_p and l are the molar heat capacity and the coefficient of thermal expansion respectively:

$$C_p = \frac{1}{\nu} \left(\frac{\delta H}{\delta T} \right)_{p, \xi} \quad (46)$$

$$l = \frac{1}{V} \left(\frac{\delta V}{\delta T} \right)_{p, \xi} \quad (47)$$

The assumption of harmonic variation with time has only influence on the equations through the time derivatives:

$$\mathbf{y} = \mathbf{y}^0 e^{i\omega t} \quad (48)$$

gives

$$\dot{\mathbf{y}} = i\omega \mathbf{y} \quad (49)$$

Finally we shall need the equation of state, which we write as

$$\delta V = V l \delta T - V \beta_T \delta p + \mathbf{y}'^T \mathbf{y} \quad (50)$$

where β_T is the isothermal compressibility

$$\beta_T = -\frac{1}{V} \left(\frac{\delta V}{\delta p} \right)_{T, \xi} \quad (51)$$

Using eqn. (49) the equations (42), (44) and (50) are now fairly easily solved for $\frac{\delta V}{\delta p}$ (which gives neater expressions than solving for $\frac{\delta p}{\delta V}$)

$$\frac{\delta V}{\delta p} = -\frac{V \beta_T C_V}{C_p} - \frac{\nu}{RT} \mathbf{f}'^T \tilde{\mathbf{G}}' (\tilde{\mathbf{A}}' + i\omega \mathbf{E})^{-1} \tilde{\mathbf{G}}' \mathbf{f}' \quad (52)$$

where we have used

$$C_V = C_p - T \frac{l^2 V}{\beta_T \nu} \quad (53)$$

and furthermore introduced the vector

$$\mathbf{f}' = \mathbf{v}' - \frac{V l}{\nu C_p} \mathbf{h}' \quad (54)$$

\mathbf{E} denotes the identity matrix and \mathbf{A}' the matrix

$$\tilde{\mathbf{A}}' = \tilde{\mathbf{G}}' \left(\mathbf{N}' \mathbf{Z}^{-1} \mathbf{N}'^T - \nu' \nu'^T + \frac{1}{C_p R T^2} \mathbf{h}' \mathbf{h}'^T \right) \tilde{\mathbf{G}}'. \quad (55)$$

The matrix $\tilde{\mathbf{G}}'$ needs some comments, since in equation (43) we have only defined $\tilde{\mathbf{G}}'^2$. \mathbf{G}'^2 is obviously a symmetric, positive semidefinite matrix and from the definition of \mathbf{B} it can be seen that \mathbf{G}'^2 is even positive definite. Hence we have no difficulties in defining the square root as a matrix, which is also symmetric and positive definite.

Since $\tilde{\mathbf{A}}'$ is positive definite, $\tilde{\mathbf{A}}'$ has positive eigenvalues. Writing $\kappa_1(\omega)$ for the real part and $\kappa_2(\omega)$ for the imaginary part of $\frac{\delta V}{\delta p}$, we have

$$\kappa_1(\omega) = -\frac{V\beta_T C_V}{C_P} - \frac{\nu}{RT} \sum_{j=1}^{n'} \frac{\tilde{\varphi}_j'^2 \tilde{\lambda}_j}{\tilde{\lambda}_j^2 + \omega^2} \quad (56)$$

$$\kappa_2(\omega) = \frac{\nu\omega}{RT} \sum_{j=1}^{n'} \frac{\tilde{\varphi}_j'^2}{\tilde{\lambda}_j^2 + \omega^2} \quad (57)$$

where $\tilde{\varphi}_j'$ is the j' 'th component of the vector $\tilde{\varphi}'$. With \mathbf{M}' as the matrix whose columns are the eigenvectors of \mathbf{A}' (in the same order as the eigenvalues), φ' is given by

$$\varphi' = \mathbf{M}'^T \mathbf{G} \mathbf{f}'. \quad (58)$$

The general formula for the attenuation factor α , now reads (see ref. 1, p. 325)

$$\alpha = \frac{\omega \cdot \varrho}{\sqrt{2}} \left[\kappa_1(\omega) + \sqrt{\kappa_1(\omega)^2 + \kappa_2(\omega)^2} \right]^{\frac{1}{2}}. \quad (59)$$

This may be simplified, if

$$\sum_{j=1}^{n'} \tilde{\varphi}_j'^2 / \tilde{\lambda}_j << \frac{V\beta_T C_V R T}{C_P \nu} \quad (60)$$

since one then has

$$|\kappa_2(\omega)| \ll |\kappa_1(\omega)| \quad (61)$$

for all values of ω . Using this and the expression

$$c = 1/(\varrho \kappa_1(\omega)) \quad (62)$$

for the velocity of sound, which is valid in the same approximation (see ref. 1, p. 326), one gets

$$\alpha = \frac{1}{2} \frac{\omega^2}{c} \frac{C_{P\nu}}{V\beta_T C_V RT} \sum_{j=1}^{n'} \frac{\tilde{\varphi}_j^2}{\tilde{\lambda}_j^2 + \omega^2}. \quad (63)$$

The approximation (60) is equivalent to the assumption that the relative variation in the velocity of sound is small, as may be seen from (62). The problem of finding the attenuation factor as a function of frequency for a given kinetic model is now reduced to finding the square root of one matrix and diagonalizing another. These operations are easily carried on numerically, but in general case they are hard to handle theoretically. For theoretical calculations it may therefore be advantageous to leave out the reduction of the number of chemical variables introduced in the equations (35) and (37)–(41). If this is done, one gets in place of $\tilde{\mathbf{A}}'$ a matrix $\tilde{\mathbf{A}}$, which has the same eigenvalues as $\tilde{\mathbf{A}}'$, and further $n-n'$ eigenvalues equal to zero. It can, however, easily be proved that the weight factors, $\tilde{\varphi}_j^2$, corresponding to these eigenvalues are zero.

IV. Approximations

From the expressions given above (for example eq. (52) or (63)) it is in general not difficult to evaluate the implications of different types of approximations. This can normally be attained by application of relatively uncomplicated parts of the theory of matrices.

Neglecting the coupling between chemical and physical degrees of freedom corresponds to neglecting the term

$$\frac{1}{C_P RT^2} \tilde{\mathbf{G}}' \mathbf{h}' \mathbf{h}'^T \tilde{\mathbf{G}}'$$

in eq. (55). If the new eigenvalues are related to the eigenvalues of $\tilde{\mathbf{A}}'$ (given by eq. (55)) by

$$\lambda_j' = \tilde{\lambda}_j - \varepsilon_j, \quad j = 1, 2, \dots, n' \quad (64)$$

then one has for the errors, ε_j :

$$\left. \begin{aligned} \varepsilon_j &\geq 0, \quad j = 1, 2, \dots, n' \\ \sum_{j=1}^{n'} \varepsilon_j &= \frac{1}{C_P RT^2} \mathbf{h}'^T \tilde{\mathbf{G}}'^2 \mathbf{h}. \end{aligned} \right\} \quad (65)$$

If the reactions can be separated in two groups, such that reaction rates are much larger in the first group than in the second, then it is generally possible to separate them by a perturbation expansion. One should, however, be aware of the possibility that a large number of coupled reactions with approximatively equal rates may give rise to relaxation in a much wider frequency range due to the coupling between the reactions as can be seen from example 2 below.

If one wants to approximate a multistep mechanism with a spectrum corresponding to a few relaxation times then one might think of several possible methods. In the appendix is outlined a method for approximating an n -step mechanism with k relaxation times. This method has the advantage that it only involves calculating moments of the matrix $\tilde{\mathbf{A}}$ with the vector \mathbf{f} which makes it especially suited for calculations in closed form. As pointed out in the appendix it is, however, less suited for numerical calculations and one might ask whether one could not find approximations which would be more useful for numerical calculation. The answer to this is that the numerical work connected with diagonalization of the matrix $\tilde{\mathbf{A}}$ in general will be of the same order of magnitude as the work connected with calculation of the approximation and that consequently it would be rather awkward to use such an approximation in place of calculation of the exact expression.

We shall state the formulas for one and two relaxation times explicitly in order to facilitate the use of the method. Since there is no need for the reduction of the number of chemical variables, we leave it out and introduce the matrix

$$\tilde{\mathbf{K}} = \left(\mathbf{N}\mathbf{Z}^{-1}\mathbf{N}^T - \nu\nu^T + \frac{1}{C_P RT^2} \mathbf{h}\mathbf{h}^T \right). \quad (66)$$

With the notation of the appendix we now find:

$$\pi_1 = \mathbf{f}^T \tilde{\mathbf{G}}^2 \mathbf{f} \quad (67)$$

$$\left. \begin{aligned} \delta_1 &= (\mathbf{f}^T \tilde{\mathbf{G}}^2 \tilde{\mathbf{K}} \tilde{\mathbf{G}}^2 \mathbf{f}) / \pi_1 \\ &= (\mathbf{f}^T \tilde{\mathbf{G}}^2 \mathbf{N}\mathbf{Z}^{-1} \mathbf{N}^T \tilde{\mathbf{G}}^2 \mathbf{f} - (\mathbf{f}^T \tilde{\mathbf{G}}^2 \nu)^2 + (\mathbf{f}^T \tilde{\mathbf{G}}^2 \mathbf{h})^2 / (C_P RT^2)) / \pi_1 \end{aligned} \right\} \quad (68)$$

$$\pi_2 = \mathbf{f}^T \tilde{\mathbf{G}}^2 \tilde{\mathbf{K}} \tilde{\mathbf{G}}^2 \tilde{\mathbf{K}} \tilde{\mathbf{G}}^2 \mathbf{f} - \delta_1^2 \pi_1 \quad (69)$$

$$\delta_2 = (\mathbf{f}^T (\tilde{\mathbf{G}}^2 \tilde{\mathbf{K}})^3 \tilde{\mathbf{G}}^2 \mathbf{f} - 2\delta_1 \mathbf{f}^T (\tilde{\mathbf{G}}^2 \tilde{\mathbf{K}})^2 \tilde{\mathbf{G}}^2 \mathbf{f} + \delta_1^3 \pi_1) / \pi_2. \quad (70)$$

The first order approximation for the attenuation factor then becomes:

$$\alpha_1 = \frac{1}{2} \frac{\omega^2}{c} \frac{C_P \nu}{V \beta_T C_V RT} \frac{\pi_1}{\delta_1^2 + \omega^2} \quad (71)$$

with the relative error:

$$\varepsilon_1 = \pi_2 / (\pi_1 \delta_1^2) \quad (72)$$

while the second order approximation may be written

$$\alpha_2 = \alpha_1 \left(1 + \frac{\pi_2}{\pi_1} \cdot \frac{\delta_1(\delta_1 + \delta_2) + (\delta_1 \delta_2 - \frac{\pi_2}{\pi_1} - \omega^2)}{(\delta_1 \delta_2 - \pi_2 / \pi_1 - \omega^2)^2 + (\delta_1 + \delta_2)^2 \omega^2} \right). \quad (73)$$

V. An alternative set of formulas

If one wants the formulas with concentrations in place of molar fractions, then one has the rate equations (10) and the equilibrium condition (12). We will write the condition (19) as

$$\frac{1}{V} \mathbf{v} = \eta \boldsymbol{\nu}. \quad (74)$$

Where η is a function of p , T , ξ (for ideal gases one has $\eta = 1/\nu$). The linearized rate equation then reads:

$$\dot{\mathbf{y}} = \mathbf{G}'^2 \left[\frac{V}{RT^2} \delta T \mathbf{h}' - \frac{V^2 \eta}{RT} \delta p \boldsymbol{\nu} + (V \eta \boldsymbol{\nu}' \boldsymbol{\nu}'^T - \mathbf{N}' \mathbf{C}^{-1} \mathbf{N}^T) \mathbf{y} \right] \quad (75)$$

with the following definitions

$$\mathbf{C} = \begin{Bmatrix} c_1 & 0 & 0 & \dots & 0 \\ 0 & c_2 & 0 & \dots & 0 \\ 0 & 0 & c_3 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & c_m \end{Bmatrix} \quad (76)$$

$$\mathbf{G}'^2 = \mathbf{B}^T \mathbf{G}^2 \mathbf{B} \quad (77)$$

$$\mathbf{G} = \begin{Bmatrix} \gamma_1 & 0 & 0 & \dots & 0 \\ 0 & \gamma_2 & 0 & \dots & 0 \\ 0 & 0 & \gamma_3 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & \gamma_n \end{Bmatrix} \quad (78)$$

$$\gamma_j^2 = k_j \prod_{k=1}^m c_k^{\nu_{jk}^+}. \quad (79)$$

The only changes in the formulas for the attenuation factor are that $\tilde{\mathbf{G}}'$ is replaced by \mathbf{G}' , $\tilde{\mathbf{A}}'$ is replaced by

$$\mathbf{A}' = \mathbf{G}' \left(\mathbf{N}' \mathbf{C}^{-1} \mathbf{N}'^T - V \eta \mathbf{v}' \mathbf{v}'^T + \frac{V}{\nu C_P R T^2} \mathbf{h}' \mathbf{h}'^T \right) \mathbf{G}' \quad (80)$$

ν is replaced by V , and the formula for \mathbf{f}' alternatively may be written:

$$\mathbf{f}' = V \eta \mathbf{v}' - \frac{V l}{\nu C_P} \mathbf{h}'. \quad (81)$$

Leaving out the tildes on the new λ 's and φ 's formula (63) reads:

$$\alpha = \frac{1}{2} \frac{\omega^2}{c} \frac{C_P}{\beta_T C_V R T} \sum_{j=1}^n \frac{\varphi_j^2}{\lambda_j^2 + \omega^2}. \quad (82)$$

Similar changes should of course be introduced in the approximation formulas (66)–(73).

VI. Examples

Three examples will be given below to show the application of the formulas and to illustrate some important implications of the theory. In the examples the formulas with concentrations will be used (eqs. 74–82)). The parameter η introduced in equation (74) will be put equal to zero.

Example 1

Consider the two chemically independent reactions



One then has for the vectors and matrices:

$$\mathbf{N} = \begin{Bmatrix} -1, 1, & 0, 0 \\ 0, 0, & -1, 1 \end{Bmatrix} \quad (84)$$

$$\gamma_1^2 = k_1 c_1; \quad \gamma_2^2 = k_2 c_3 \quad (85)$$

$$\mathbf{h}^T = \{h_1, h_2\} \quad (86)$$

$$\mathbf{A} = \begin{Bmatrix} k_1 + k_{-1} + \mathcal{H}_1^2, & \mathcal{H}_1 \mathcal{H}_2 \\ \mathcal{H}_1 \mathcal{H}_2, & k_2 + k_{-2} + \mathcal{H}_2^2 \end{Bmatrix} \quad (87)$$

with:

$$\left. \begin{aligned} \mathcal{H}_1 &= \gamma_1 h_1 \sqrt{V / (\nu C_P R T^2)} \\ \mathcal{H}_2 &= \gamma_2 h_2 \sqrt{V / (\nu C_P R T^2)} \end{aligned} \right\} (88)$$

The eigenvalues of \mathbf{A} become:

$$\left. \begin{aligned} \lambda_1 \\ \lambda_2 \end{aligned} \right\} = \frac{1}{2} (\lambda_1^0 + \lambda_2^0 \pm \sqrt{(\lambda_1^0 - \lambda_2^0)^2 - 4 \mathcal{H}_1^2 \mathcal{H}_2^2}) \quad (89)$$

$$\left. \begin{aligned} \lambda_1^0 &= k_1 + k_{-1} + \mathcal{H}_1^2 \\ \lambda_2^0 &= k_2 + k_{-2} + \mathcal{H}_2^2 \end{aligned} \right\} (90)$$

It is seen that the eigenvalues corresponding to two reactions (λ_1^0 and λ_2^0) are perturbed even though the two reactions are chemically independent. This effect is important if one uses a solvent with a relaxation time near the relaxation time of the solute one is investigating. It will normally not be correct merely to subtract the background in that case.

The maximal effect is obtained with

$$\lambda_1^0 = \lambda_2^0 = \lambda^0. \quad (91)$$

In this case one gets:

$$\left. \begin{aligned} \lambda_1 &= \lambda^0 + \mathcal{H}_1 \mathcal{H}_2 \\ \lambda_2 &= \lambda^0 - \mathcal{H}_1 \mathcal{H}_2 \end{aligned} \right\} (92)$$

$$\mathbf{M} = \frac{1}{\sqrt{2}} \begin{Bmatrix} 1, & 1 \\ 1, & -1 \end{Bmatrix} \quad (93)$$

$$\left. \begin{aligned} \varphi_1^2 &= \frac{1}{2} (Vl/(\nu C_P))^2 (\gamma_1 h_1 + \gamma_2 h_2)^2 \\ \varphi_2^2 &= \frac{1}{2} (Vl/(\nu C_P))^2 (\gamma_1 h_1 - \gamma_2 h_2)^2. \end{aligned} \right\} (94)$$

The formula for φ for a single reaction is

$$\varphi^2 = (Vl/(\nu C_P))^2 (\gamma h)^2. \quad (95)$$

The value of α/ω^2 found if one subtracts the background (only the first reaction) from the measured value with both reactions is then, aside from a constant factor, given by

$$\frac{\alpha}{\omega^2} = \frac{1}{2} \frac{(\mathcal{H}_1 + \mathcal{H}_2)^2}{\lambda_1^2 + \omega^2} + \frac{1}{2} \frac{(\mathcal{H}_1 - \mathcal{H}_2)^2}{\lambda_2^2 + \omega^2} - \frac{\mathcal{H}_1^2}{(\lambda^0)^2 + \omega^2} \quad (96)$$

while the correct value corresponding to the second reaction is

$$\frac{\alpha}{\omega^2} = \frac{\mathcal{H}_2^2}{(\lambda^0)^2 + \omega^2}. \quad (97)$$

The two curves are shown in figure 1.

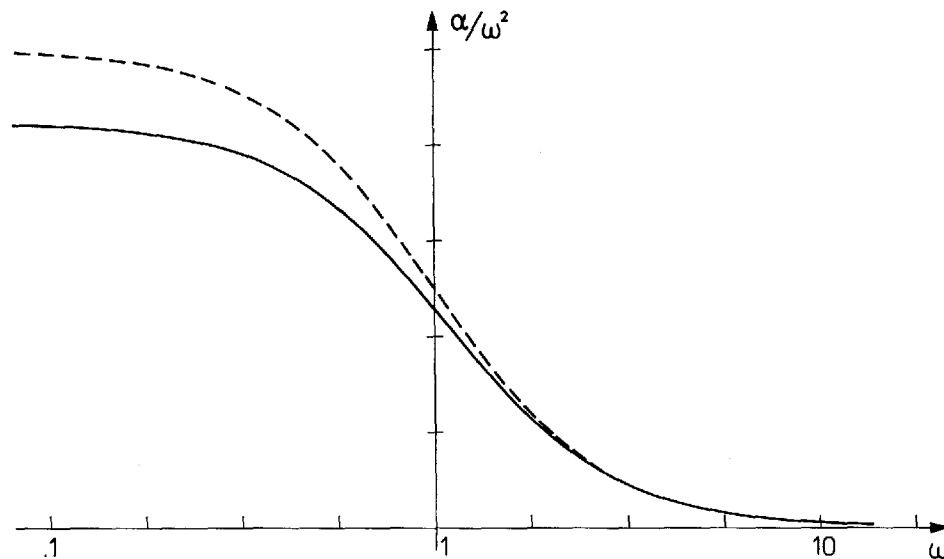
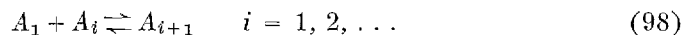


Figure 1 shows α/ω^2 as a function of $\log(\omega)$ corresponding to the eqs. (96) (—) and (97) (---) for $\mathcal{H}_1 = \mathcal{H}_2 = 0.2$.

Example 2

Consider the polymerization scheme:



If it is assumed that all reactions have the same equilibrium constant, K , the same rate constants, k^+ and k^- , and the same change in enthalpy, ΔH , then one has

$$\zeta = Kc_1 \quad (99)$$

$$c_i = \zeta^{i-1}c_1 \quad (100)$$

$$\gamma_i^2 = k^-c_1\zeta^i \quad (101)$$

$$\mathbf{h} = \Delta H\mathbf{e} \quad (102)$$

$$\nu_{ij} = -\delta_{1,j} - \delta_{j,i} + \delta_{j,i+1} \quad (103)$$

$$\left. \begin{aligned} a_{ij} &= \gamma_i\gamma_j \left[c_1^{-1}(\delta_{j,1} + \delta_{i,1} + 1 + \mathcal{H}^2) \right. \\ &\quad \left. + \delta_{i,j}(c_i^{-1} + c_{i+1}^{-1}) - \delta_{i+1,j}c_j^{-1} - \delta_{i,j+1}c_i^{-1} \right] \\ &= k^- \left[\zeta^{\frac{1}{2}(i+j)} (\delta_{j,1} + \delta_{i,1} + 1 + \mathcal{H}^2) \right. \\ &\quad \left. + \delta_{i,j}(\zeta + 1) - (\delta_{i,j+1} + \delta_{i+1,j})\zeta^{\frac{1}{2}} \right] \end{aligned} \right\} \quad (104)$$

$$\mathcal{H}^2 = c_1 \cdot V \cdot \Delta H^2 / (\nu C_P RT^2) \quad (105)$$

where $\delta_{i,j}$ is the Kronecker delta.

Applying the approximation method of the appendix one finds:

$$\left. \begin{aligned} \pi_1 &= k^-c_1 (\Delta H \cdot V \cdot l / (\nu C_P))^2 \sum_{j=1}^{\infty} \zeta_j \\ &= k^-c_1 (\Delta H \cdot V \cdot l / (\nu C_P))^2 \zeta / (1 - \zeta) \end{aligned} \right\} \quad (106)$$

$$\delta_1 = (1 + \zeta + (1 + \mathcal{H}^2)\zeta / (1 - \zeta)) \cdot k^- \quad (107)$$

$$\pi_2 = \pi_1 \zeta / (1 - \zeta) \quad (108)$$

$$\delta_2 = k^-(1 + \zeta). \quad (109)$$

Fig. 2 and 3 show for two values of ζ the approximations with one and two relaxation times together with the exact curve (calculated by diagonalizing a sufficiently large submatrix of \mathbf{A}). The calculated eigenvalues are also shown. It is seen that the eigenvalue spectrum gets rather broad for ζ close to one and that the approximations at the same time get less satisfactory. The calculations for ζ close to one show an interesting consequence of the

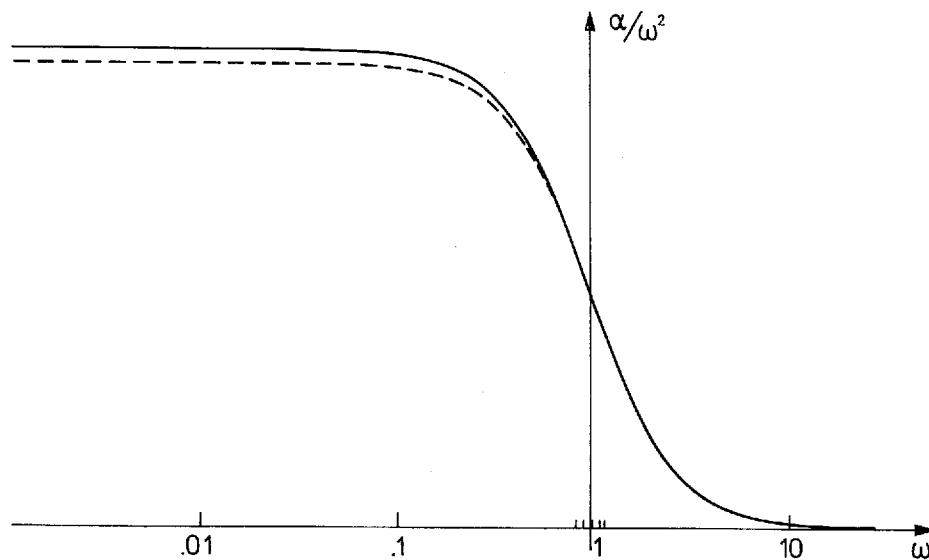


Figure 2 shows α/ω^2 as a function of $\log(\omega)$ for the reaction scheme given in example 2 with $\zeta = 0.01$ and $\mathcal{H}^2 = 0.001$ (—). Also shown is the approximation with a single relaxation time given by eqs. (71, 106, 107) (- - -). The approximation with two relaxation times cannot be distinguished from the correct curve.

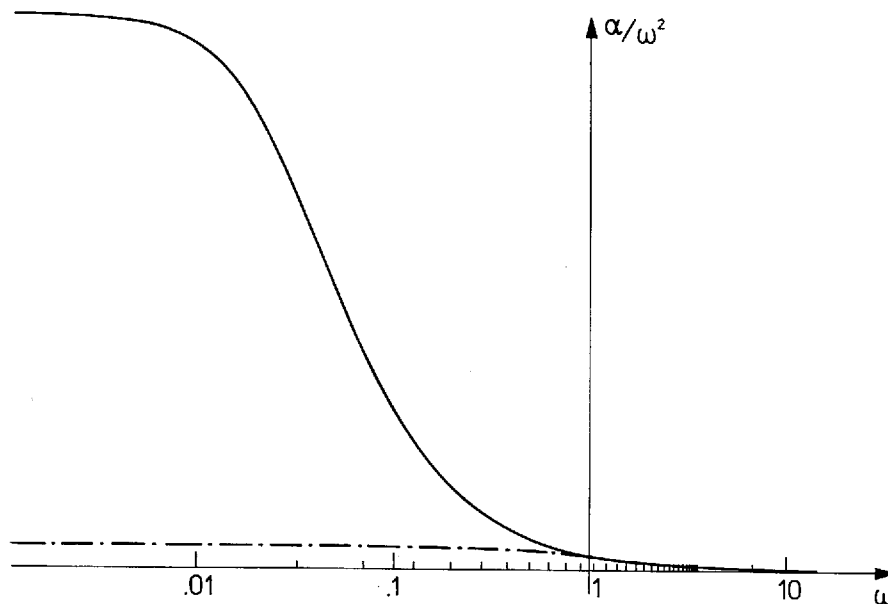


Figure 3 shows α/ω^2 as a function of $\log(\omega)$ for the reaction scheme given in example 2 with $\zeta = 0.8$ and $\mathcal{H}^2 = 0.1$ (—). Also shown is the approximation with two relaxation times, given by eqs. (73, 106-109) (- - - -). The approximation with one relaxation time cannot be distinguished from the abscisse axis.

TABLE 1.

| eigenvalue(s) | Contribution to | |
|---------------|-------------------------|--------------------------------|
| | $\alpha\omega = \infty$ | $(\alpha/\omega^2)_{\omega=0}$ |
| 0.03 | 0.006 | 6.554 |
| 0.07 | 0.011 | 2.490 |
| 0.12 | 0.017 | 1.136 |
| 0.19 | 0.019 | 0.539 |
| 0.20-0.80 | 0.121 | 0.675 |
| 0.80-2.00 | 0.159 | 0.101 |
| 2.00-3.60 | 0.115 | 0.017 |
| 6.99 | 2.749 | 0.056 |

Table I shows that the large contributions to $(\alpha/\omega^2)_{\omega=0}$ come from small eigenvalues although the corresponding values of φ_j^2 are small ($\alpha\omega = \infty$). The numbers are taken from a 31×31 matrix corresponding to the model in example 2 with $\zeta = 0.8$ and $\mathcal{H}^2 = 0.1$.

broad spectrum, which arises from the strong coupling between the single reactions. The value of α/ω^2 at $\omega = 0$ is often used to characterize the relaxation curve. This is, however, not a very suitable parameter since small changes in the kinetic model may give rise to a large change in $(\alpha/\omega^2)_{\omega=0}$. The largest contributions to $(\alpha/\omega^2)_{\omega=0}$ will normally come from small eigenvalues even if the corresponding values of φ_j^2 are small, but if \mathbf{Gf} only has a small component after a given eigenvector then it is very likely that small changes in \mathbf{A} or \mathbf{G} or \mathbf{f} may result in a large, relative change in the component.

That the largest contribution to $(\alpha/\omega^2)_{\omega=0}$ actually comes from small eigenvalues with small weights in the present case is clearly exhibited in Table I.

In view of the proceeding remarks it is not surprising that the effect of leaving out the term \mathcal{H}^2 in eq. (104) is large for ζ close to one as can be seen from Fig. 4.

Example 3

Finally an example to illustrate the reduction in case of chemical reactions which are not all independent is given. For this purpose example 2 is expanded to include all possible combinations of two molecules to one large, but only reactions up to formation of 5-mers are included in order to get a reasonable simple problem.

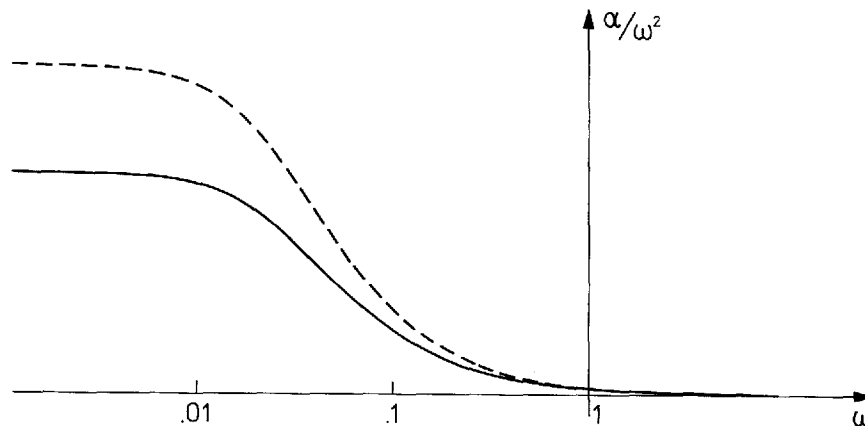
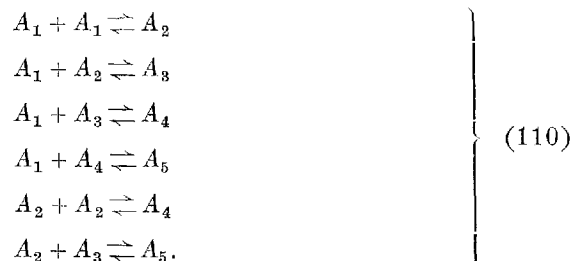


Figure 4 shows α/ω^2 as a function of $\log(\omega)$ for the reaction scheme given in example 2 with $\zeta = 0.8$ and $\kappa^2 = 0.1$ (—) and $\zeta = 0.8$ and $\kappa^2 = 0$ (- - -).

The reactions are:



The matrix \mathbf{N} becomes:

$$\mathbf{N} = \begin{Bmatrix} -2, & 1, & 0, & 0, & 0 \\ -1, & -1, & 1, & 0, & 0 \\ -1, & 0, & -1, & 1, & 0 \\ -1, & 0, & 0, & -1, & 1 \\ 0, & -2, & 0, & 1, & 0 \\ 0, & -1, & -1, & 0, & 1 \end{Bmatrix} \quad (111)$$

and the vector \mathbf{h} :

$$\mathbf{h}^T = \{\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_5, \Delta H_6\}. \quad (112)$$

The two last reactions in (110) can evidently be written as a combination of the first four reactions. The matrix \mathbf{B} is

$$B = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 1 & 1 & 0 \\ -1 & 0 & 1 & 1 \end{pmatrix} \quad (113)$$

while the matrix \mathbf{N}' is identical with the first four rows of \mathbf{N} , and the vector \mathbf{h}' is identical with the first four elements of \mathbf{h} . One has the thermodynamic relations:

$$\Delta H_5 = -\Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_6 = -\Delta H_1 + \Delta H_3 + \Delta H_4$$

$$K_5 = K_2 K_3 / K_1$$

$$K_6 = K_3 K_4 / K_1.$$

The matrix \mathbf{G}'^2 becomes

$$\mathbf{G}'^2 = \begin{pmatrix} \gamma_1^2 + \gamma_5^2 + \gamma_6^2, & -\gamma_5^2, & -\gamma_5^2 - \gamma_6^2, & -\gamma_6^2 \\ -\gamma_5^2, & \gamma_2^2 + \gamma_5^2, & \gamma_5^2, & 0 \\ -\gamma_5^2 - \gamma_6^2, & \gamma_5^2, & \gamma_3^2 + \gamma_5^2 + \gamma_6^2, & \gamma_6^2 \\ -\gamma_6^2, & 0, & \gamma_6^2, & \gamma_4^2 + \gamma_6^2 \end{pmatrix} \quad (114)$$

Acknowledgement

The author is indebted to Professor Thor A. Bak for his stimulating interest in this work. The author is also very indebted to lic. pharm. Jørgen Rassing for many interesting discussions which helped the author greatly in understanding which part of the theory was relevant to the experimentalists.

Appendix

The problem is to find a series of approximations to an expression of the form

$$\psi^H (\mathbf{A} + i\omega \mathbf{E})^{-1} \psi \quad (\text{A. 1})$$

where ψ is an n -dimensional vector and \mathbf{A} is an $n \times n$ -matrix.

We shall start by transforming \mathbf{A} into a traditional matrix by Lanczo's algorithm for tridiagonalization (see ref. 4, p. 19). We generate two sequences of vectors

$$\mathbf{b}_1, \mathbf{b}_2, \dots, \mathbf{b}_n \quad (\text{A. 2})$$

$$\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_n \quad (\text{A. 3})$$

which fulfils:

$$\mathbf{c}_i^H \mathbf{b}_j = \delta_{i,j} \pi_j \quad \pi_j \neq 0 \quad (\text{A. 4})$$

and where the first ν is determined by ($\gamma_1 = 0$):

$$\mathbf{c}_1 = \mathbf{b}_1 = \boldsymbol{\psi} \quad (\text{A. 5})$$

$$\mathbf{b}_{j+1} = \mathbf{A}\mathbf{b}_j - \delta_j \mathbf{b}_j - \gamma_j \mathbf{b}_{j-1} \quad (\text{A. 6})$$

$$\mathbf{c}_{j+1} = \mathbf{A}^H \mathbf{c}_j = \delta_j^* \mathbf{c}_j - \gamma_j \mathbf{c}_{j-1} \quad (j = 1, 2, \dots, \nu - 1) \quad (\text{A. 7})$$

(*stands for complex conjugate). ν is determined as the lowest value for which it is possible to get at least one of the following equations fulfilled

$$\mathbf{A}\mathbf{b}_\nu = \delta_\nu \mathbf{b}_\nu + \gamma_\nu \mathbf{b}_{\nu-1} \quad (\text{A. 8})$$

$$\mathbf{A}^H \mathbf{c}_\nu = \delta_\nu^* \mathbf{c}_\nu + \gamma_\nu \mathbf{c}_{\nu-1}. \quad (\text{A. 9})$$

The remaining $n-\nu$ vectors \mathbf{b} and \mathbf{c} can be chosen to be any vectors such that (A. 4) is fulfilled for all i and j .

$$\delta_j = \mathbf{c}_j^H \mathbf{A} \mathbf{b}_j / \pi_j, \quad j \geq 1 \quad (\text{A. 10})$$

$$\gamma_j = \pi_j / \pi_{j-1}, \quad j \geq 2. \quad (\text{A. 11})$$

With \mathbf{B} and \mathbf{C} as the matrices

$$\mathbf{B} = \{\mathbf{b}_1, \mathbf{b}_2, \dots, \mathbf{b}_n\} \quad (\text{A. 12})$$

$$\mathbf{C} = \{\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_n\} \quad (\text{A. 13})$$

and \mathbf{P} as the diagonal matrix whose diagonal elements are the π_j 's, (A. 4) may be written

$$\mathbf{B}^{-1} = \mathbf{P}^{-1} \mathbf{C}^H \quad (\text{A. 14})$$

The similarity transformation:

$$\mathbf{P}^{-1} \mathbf{C}^H \mathbf{A} \mathbf{B} = \mathbf{A}' \quad (\text{A. 15})$$

will transform (1) into:

$$\mathbf{e}_1^T (\mathbf{A}' + i\omega \mathbf{E})^{-1} \mathbf{e}_1 \cdot \pi_1 \quad (\text{A. 16})$$

$$\mathbf{e}_1^T = \{1, 0, 0, \dots, 0\}. \quad (\text{A. 17})$$

If \mathbf{A}' is partitioned:

$$\mathbf{A}' = \begin{Bmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} \\ \mathbf{A}_{21} & \mathbf{A}_{22} \end{Bmatrix} \quad (\text{A. 18})$$

Where \mathbf{A}_{11} is $\nu \times \nu$, one has

$$\mathbf{A}_{11} = \begin{Bmatrix} \delta_1 & \gamma_2 & 0 & \dots & 0 \\ 1 & \delta_2 & \gamma_3 & & 0 \\ 0 & 1 & \delta_3 & & 0 \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ 0 & 0 & 0 & & \delta_\nu \end{Bmatrix} \quad (\text{A. 19})$$

while either \mathbf{A}_{12} or \mathbf{A}_{21} is zero depending on whether (A. 9) or (A. 8) is fulfilled. (A. 16) is consequently reduced to:

$$\mathbf{e}_1^T (\mathbf{A}_{11} + i\omega \mathbf{E})^{-1} \mathbf{e}_1 \cdot \pi_1 \quad (\text{A. 20})$$

We will now return to the original problem. This may be viewed as the problem of finding approximate solutions to the equation:

$$(\mathbf{A} + i\omega \mathbf{E})\mathbf{x} = \boldsymbol{\psi}. \quad (\text{A. 21})$$

A series of successive approximations to \mathbf{x} can be obtained by using the residual of the preceding approximation to determine the next approximation. This gives the general recursion formula:

$$\mathbf{x}_k = \mathbf{x}_{k-1} + \mathbf{C}_k(\boldsymbol{\psi} - (\mathbf{A} + i\omega \mathbf{E})\mathbf{x}_{k-1}). \quad (\text{A. 22})$$

(see ref. 4, p. 92 ff.), where the matrices \mathbf{C}_k should be chosen so that the "error" is minimized. The error on \mathbf{x}_k is given by:

$$\mathbf{x} - \mathbf{x}_k = \mathbf{s}_k = (\mathbf{E} - \mathbf{C}_k(\mathbf{A} + i\omega \mathbf{E}))\mathbf{s}_{k-1}. \quad (\text{A. 23})$$

If one starts the sequence (A. 22) with

$$\mathbf{x}_0 = \mathbf{0} \quad (\text{A. 24})$$

One gets:

$$\mathbf{s}_k = \left[\prod_{j=1}^k (\mathbf{E} - \mathbf{C}_j(\mathbf{A} + i\omega \mathbf{E})) \right] \mathbf{x}. \quad (\text{A. 25})$$

Since we want to find $\boldsymbol{\psi}^H \mathbf{x}$, it will be reasonable to try to minimize $\boldsymbol{\psi}^H \mathbf{s}_k$, or since \mathbf{x} is not known

$$\left| \boldsymbol{\psi}^H \prod_{j=1}^k (\mathbf{E} - \mathbf{C}_j(\mathbf{A} + i\omega \mathbf{E})) \mathbf{x}_k \right|. \quad (\text{A. 26})$$

We now have to choose the form of our matrices, \mathbf{C}_j ($j = 1, 2, \dots, k$), and we choose them as simple as possible:

$$\mathbf{C}_j = \frac{1}{\xi_j} \mathbf{E}. \quad (\text{A. 27})$$

From the recursion formula (A. 22) and the initializing (A. 24), it is easily seen that (A. 26) only depends on $\mathbf{A} + i\omega \mathbf{E}$ and $\boldsymbol{\psi}$ through the moments

$$\mu_j = \boldsymbol{\psi}^H (\mathbf{A} + i\omega \mathbf{E})^j \boldsymbol{\psi} \quad (j = 0, 1, \dots, 2k-1). \quad (\text{A. 28})$$

Using now the expression (A. 20), one has from the special form (A. 19) of \mathbf{A}_{11} , that the moments

$$\mu'_j = \mathbf{e}_1^T (\mathbf{A}_{11} + i\omega \mathbf{E})^j \mathbf{e}_1 \quad (j = 0, 1, \dots, 2k-1) \quad (\text{A. 29})$$

are the same as they are for the matrix $\mathbf{A}_{11}^{(k)} + i\omega \mathbf{E}$, where we have only kept the first k columns and rows of $\mathbf{A}_{11} + i\omega \mathbf{E}$.

The approximation \mathbf{x}_k will be exact for the equation:

$$(\mathbf{A}_{11}^{(k)} + i\omega \mathbf{E}) \mathbf{x} = \mathbf{e}_1 \quad (\text{A. 30})$$

if we make the choice

$$\xi_j = \lambda_j^{(k)} + i\omega \quad (\text{A. 31})$$

where $\lambda_j^{(k)}$ is the j 'th eigenvalue of $\mathbf{A}_{11}^{(k)}$. And we consequently have that the same choice make the expression (A. 26) for the error equal to zero. The k 'th order approximation to (A. 1) can now be written

$$\boldsymbol{\psi}^H (\mathbf{A} + i\omega \mathbf{E})^{-1} \boldsymbol{\psi} \simeq \pi_1 \sum_{j=1}^k \frac{\alpha_j^{(k)}}{\lambda_j^{(k)} + i\omega} \quad (\text{A. 32})$$

$\alpha_j^{(k)}$ is the product of the first component of the j 'th eigenvector to $\mathbf{A}_{11}^{(k)}$ from the right with the first component of the j 'th eigenvector to $\mathbf{A}_{11}^{(k)}$ from the left.

It is, however, possible to give (A. 32) a form which is more convenient

for many purposes. Writing D_j for the determinant of $v-j$ last row and columns of $\mathbf{A}_{11} + i\omega\mathbf{E}$, one has

$$\left. \begin{aligned} e_1^T (\mathbf{A}_{11} + i\omega\mathbf{E})^{-1} e_1 &= \frac{D_1}{D_0} = \\ \frac{1}{\delta_1 + i\omega - \gamma_2 \frac{D_2}{D_1}} &= \frac{1}{\delta_1 + i\omega - \gamma_2} \delta_2 + i - \frac{\gamma_3}{\gamma_3 + i - \dots} \dots \end{aligned} \right\} \text{(A. 33)}$$

This continued fraction can be transformed into a sum of fractions (ref. 5 p. 5):

$$\psi^H (\mathbf{A} + i\omega\mathbf{E})^{-1} \psi = \frac{\pi_1}{Q_0 Q_1} + \frac{\pi_2}{Q_1 Q_2} + \dots + \frac{\pi_v}{Q_{v-1} Q_v} \quad \text{(A. 34)}$$

with the Q 's given by the recursion formula

$$\left. \begin{aligned} Q_j &= (\delta_j + i\omega) Q_{j-1} - \gamma_j Q_{j-2} \\ Q_{-1} &= 0, Q_0 = 1 \end{aligned} \right\} \text{(A. 35)}$$

The k 'th order approximation (A. 32) will be identical with the first k terms of (A. 35). In order to estimate the error on the k 'th approximation one can of course not use (A. 26). If one supposes that the following terms drop off reasonable fast one may use the $k+1$ 'th term in (A. 34) for estimating the error. A rough estimate of Q_j in the range of ω which is of interest may be found by assuming that all the δ 's are of the same order of magnitude as ω (and that the γ 's do not blow up):

$$|Q_j| \approx \omega^j \approx \delta_1^j \quad \text{(A. 36)}$$

which gives for the relative error on the k 'th approximation

$$\varepsilon_k \approx \frac{\pi_{k+1}}{\pi_1 \delta_1^{2k}} \quad \text{(A. 37)}$$

Applicability of the method: Obviously the method applies to any expression of the form

$$\psi^H (\mathbf{A} + f(\omega)\mathbf{E})^{-1} \psi \quad \text{(A. 38)}$$

where $f(\omega)$ is a complex function. This might be used to find other similar approximations to the expression (A. 1), since one can rewrite (A. 1) as

$$\left. \begin{aligned} \operatorname{Re} \{ \psi^H (\mathbf{A} + i\omega \mathbf{E})^{-1} \psi \} = \\ (\mathbf{A}^{\frac{1}{2}} \psi)^H (\mathbf{A}^2 + \omega^2 \mathbf{E})^{-1} (\mathbf{A}^{\frac{1}{2}} \psi) \end{aligned} \right\} \text{(A. 39)}$$

$$\left. \begin{aligned} \operatorname{Im} \{ \psi^H (\mathbf{A} + i\omega \mathbf{E})^{-1} \psi \} = \\ - \omega \psi^H (\mathbf{A}^2 + \omega^2 \mathbf{E})^{-1} \psi \end{aligned} \right\} \text{(A. 40)}$$

$$\left. \begin{aligned} \psi^H (\mathbf{A} + i\omega \mathbf{E})^{-1} \psi = \\ (\mathbf{A}^{-\frac{1}{2}} \psi)^H (\mathbf{A}^{-1} - (i/\omega) \mathbf{E})^{-1} (\mathbf{A}^{-\frac{1}{2}} \psi). \end{aligned} \right\} \text{(A. 41)}$$

The method of tridiagonalization can easily be generalized to expressions of the form

$$\psi^H (\mathbf{A} + f(\omega) \mathbf{E})^{-1} \varphi \quad \text{(A. 42)}$$

where ψ and φ any two n -dimensional vectors which are not orthogonal, i.e.:

$$\psi^H \varphi \neq 0 \quad \text{(A. 43)}$$

However, one warning should be given: Lanczo's method of tridiagonalization is in general not numerically stable, and the method should consequently in connection with numerical calculations only be used for calculating approximations of low order ($k = 1$ or 2).

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