

Oscillations, multiple steady states, and instabilities in illuminated systems*

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The absorption of light by some but not all species of a chemical reaction, followed by a radiationless transition and ultimate conversion of light into heat on a time scale short compared to the chemical reaction time scale, is shown to give rise to the possibilities of multiple steady states, damped oscillations in state variables, hysteresis, and instabilities. All these phenomena are predicted to occur even for the simplest reaction $A \rightleftharpoons B$, where only A absorbs light, and where the rate equation, with temperature dependent rate coefficients, is coupled nonlinearly to the equation for the rate of change of temperature. The theory is developed for both stationary and transient experiments. For the cyclic reaction mechanism $A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons A$, where again only A absorbs light, damped oscillations occur under isothermal conditions; the illumination, as described, effectively breaks microscopic reversibility. Both the kinetic and the thermodynamic analysis show the essential role of light in effectively breaking microscopic reversibility analogous to the net flux of reactants and of products across the boundary of an open system. In nonequilibrium relaxation experiments performed on illuminated systems with damped oscillations, both a frequency and a decay rate may be measured. The application of periodic perturbations leads to resonance effects.

I. INTRODUCTION

Chemical instabilities have been shown to occur in reaction mechanisms which are maintained far from chemical equilibrium and which involve some type of feedback.¹⁻⁴ In most of the mechanisms proposed to account for observed instabilities, multiple stationary states and oscillations in chemical and biochemical systems, nonequilibrium conditions are maintained by continuous addition of reactants and removal of products. Possible feedback mechanisms include homogeneous autocatalysis,^{1,2} nonlinearities in kinetic coefficients,^{1,2} variable membrane permeabilities,⁵ configuration changes and cooperative effects.⁶ An example of the second kind is the nonlinearities caused by the interaction of enthalpy changes with temperature dependent rate coefficients in adiabatic systems.^{7,8} Whenever thermal conductivity is small relative to the rate of heat production during the reaction, nonlinear effects of this kind may drive the system unstable provided that it is maintained far enough from equilibrium. This problem is of interest in chemical engineering and has been studied in relation to the question of thermal stability of chemical reactors.⁷

In this paper we investigate the role of light in inducing oscillations, multiple stationary states, and instabilities in chemical systems. We consider the effects of light absorbed by a system such that the system is maintained in a nonequilibrium steady or transient state. Light has been previously used in a similar manner to produce and maintain a nonequilibrium concentration of charge carriers in semiconductors.⁹ Instabilities in current flow are then caused in this case by a nonlinear depen-

dence of the rate of capture of these carriers on the external electric field.⁹

In Sec. II we analyze the simple example of an isomerization reaction in which only one of the isomers absorbs light of a given frequency followed by rapid irreversible conversion of electronic energy into heat. The absorption of light causes an asymmetric displacement of the isomerization from equilibrium since the light absorption is proportional to the density of the absorbing molecule which in turn is coupled nonlinearly to the reaction through the temperature dependence of the rate coefficients. The thermodynamic analysis of such systems, as in Sec. III, shows the necessity for the asymmetric displacement from equilibrium for observing the cited effects, which is equivalent to incorporating a process with the function of breaking microscopic reversibility. In Sec. IV we discuss the effect of light absorbed by one species only in a cyclic isothermal isomerization of three species. We conclude in Sec. V with a discussion of some possible applications.

II. LIGHT INDUCED INSTABILITIES IN A THERMOCHEMICAL SYSTEM

A. A Model Experiment

Consider a system in which a reaction



is taking place which is illuminated by a constant uniform monochromatic light of a wavelength which is absorbed by A alone (Fig. 1). The entire system heats up due to the conversion of light energy into heat by radiationless relaxation processes.

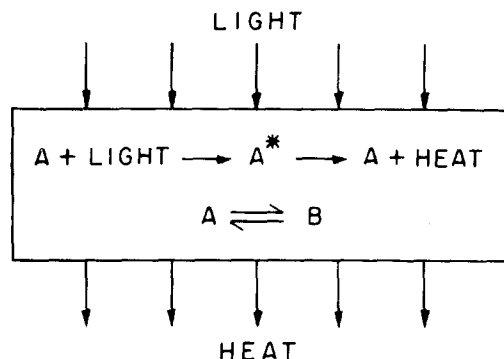


FIG. 1. A schematic description of the experimental system.

The system loses heat due to thermal contact with a surrounding bath at constant temperature. After a time interval, the system is in a stationary state. We are now interested in the stability of this state: When will fluctuations from this reference state increase in time; when will they decay monotonically or with oscillations? The experimental answer to these questions is generally obtained by studying the system's response to an external perturbation. We may apply a sudden perturbation on a steady-state system or on a temporally evolving system during its heating up period and follow the response in the temperature or the concentrations. Alternatively continuous methods such as light scattering or oscillatory variation of the rate coefficients may be employed.

B. Theory

The system described is analyzed with the following assumptions:

(i) The light absorption and the subsequent radiationless relaxation processes occur on a time scale much shorter than that for the $A \rightleftharpoons B$ reaction.

(ii) The radiationless relaxation processes are fast relative to the optical excitation and deexcitation ($A + h\nu \rightleftharpoons A^*$) rates, and to the rate of the $A^* \rightarrow B$ reaction, so that the modification of the rate coefficients due to this last reaction may be disregarded. The rate coefficients k_1 , k_2 , thus depend on the illumination only through the temperature variation.

(iii) The temperature dependence of the rate coefficients is taken to be of the simple Arrhenius type

$$k_i(T) = \kappa_i \exp(-R_i/T); \quad i = 1, 2, \quad (\text{II. 1})$$

where T is the absolute temperature and κ is assumed for simplicity to be constant. The activation energy for the reaction is expressed here in degrees Kelvin; the enthalpy change expressed in the same

units is

$$\Delta H = R_2 - R_1. \quad (\text{II. 2})$$

(iv) The system is homogeneous in both concentrations and temperature. This may be experimentally achieved by an efficient stirring, or, when fast reactions are studied, by homogeneously distributing the light beam over the system.¹⁰ If a transient experiment is performed the time scale may be chosen such that the measurement is done when inhomogeneities due to the relatively slow heat conduction have not been yet developed.

(v) The cooling rate of the system is linear in the temperature difference between the system and its surrounding bath.

For assumptions (1) and (2) to hold, the molecule A should be large enough with intra- and intermolecular interactions strong enough to provide very fast electronic and vibrational radiationless relaxation processes. For large molecules, and also for solvated metal ions which behave similarly, the time scale for the $A^* \rightarrow (A + \text{heat})$ relaxation may be as short as 10^{-12} sec in liquids, or 10^{-9} sec in gases. Assumptions (3)–(5) are made for mathematical simplicity only and more elaborate models can be studied by methods identical to that used here.

With the aid of these assumptions the kinetic equations which govern the time evolution and the stability properties of the system may be written in the form

$$dA/dt = -(k_1 + k_2)A + k_2a, \quad (\text{II. 3a})$$

$$dT/dt = \alpha A - \beta(T - T_\theta) - \lambda dA/dt. \quad (\text{II. 3b})$$

The symbols denote: $A + B = a = \text{constant}$; α is a constant proportional to the light intensity and the absorption coefficient; β is a constant which corresponds to the cooling rate of the system; and T_θ is the constant external temperature. Finally, λ is the temperature variation due to the enthalpy change which in terms of the activation energies R_1 and R_2 is

$$\lambda = (R_2 - R_1)/\epsilon, \quad (\text{II. 4})$$

where ϵ is a constant proportional to the heat capacity of the system. (For a system having heat capacity of ~ 1 kcal/deg, $\epsilon \sim 500$ mole.) Our first step in studying the mathematical properties of the system (II. 3) will be concerned as usual with its steady-state solutions.

C. Steady State Analysis

When all the time derivatives vanish there result the equations for the steady state

$$A = k_2a/(k_1 + k_2), \quad (\text{II. 5a})$$

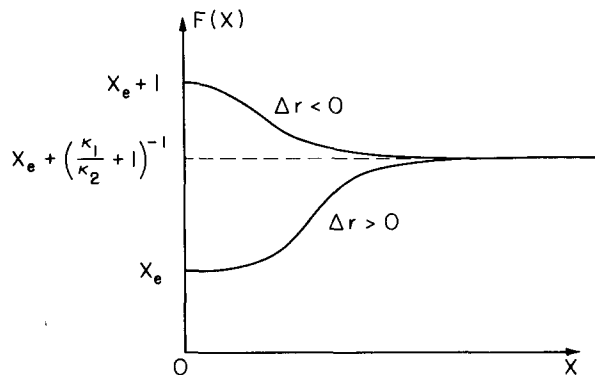


FIG. 2. A schematic representation of the function $F(X)$ [Eq. (II.9)]. X_e , κ_1 , κ_2 , and Δr are defined in the text.

$$T = T_e + \alpha A / \beta. \tag{II. 5b}$$

The steady state temperature is thus the solution T_0 of the equation

$$T_0 = T_e + (\alpha A / \beta) [(\kappa_1 / \kappa_2) \exp(\Delta R / T_0) + 1]^{-1} \tag{II. 6}$$

with $\Delta R = R_2 - R_1$. Defining the dimensionless variables

$$X = T\beta / \alpha a; X_e = T_e(\beta / \alpha a); \Delta r = \Delta R(\beta / \alpha a) \tag{II. 7}$$

we have for the steady state equation (II. 6)

$$X_0 = F(X_0) \tag{II. 8}$$

with

$$F(X) = [(\kappa_1 / \kappa_2) \exp(\Delta r / X) + 1]^{-1} + X_e. \tag{II. 9}$$

A schematic representation of the function $F(X)$ is given in Fig. 2. $F(X)$ is monotonically increasing from $F(X) = X_e$ at $X = 0$ to $F(X) \rightarrow X_e + [(\kappa_1 / \kappa_2) + 1]^{-1}$ at $X \rightarrow \infty$ for $\Delta r > 0$, and is monotonically decreasing from $F(X) = X_e + 1$ at $X = 0$ to $F(X) \rightarrow X_e + [(\kappa_1 / \kappa_2) + 1]^{-1}$ at $X \rightarrow \infty$ for $\Delta r < 0$. By inspection we see that for $\Delta r < 0$ one and only one crossing point with the straight line $y = X$ exists while for $\Delta r > 0$ one or three solutions are possible for Eq. (II. 8). The last possibility results from the fact that $F(X)$ has an inflection point X_m , at which the function

$$F'(X) = \frac{(\kappa_1 / \kappa_2) (\Delta r / X^2) \exp(\Delta r / X)}{[(\kappa_1 / \kappa_2) \exp(\Delta r / X) + 1]^2} \tag{II. 10}$$

assumes its extremal value. (Note that $F'(0) = F'(\infty) = 0$ which implies at least one such extremum.) From $F''(X_m) = 0$ we get the following equation for X_m

$$\exp(\Delta r / X_m) = \frac{\kappa_2 (\Delta r / X_m) + 2}{\kappa_1 (\Delta r / X_m) - 2} \tag{II. 11}$$

which has only a single solution. The occurrence of only one inflection point makes it impossible for more than three steady states to exist for given parameters T_e and Δr .

A straightforward analysis of Eqs. (II. 9) and (II. 10) (Appendix A) leads to the following necessary conditions for multiple (three) steady states:

$$R_2 > R_1 \text{ (exothermic A - B reaction),} \tag{II. 12a}$$

$$F'(X_m) > 1, \tag{II. 12b}$$

$$(\alpha A / \beta) (\Delta r / T^2) \frac{(\kappa_1 / \kappa_2) \exp(\Delta R / T)}{[(\kappa_1 / \kappa_2) \exp(\Delta R / T) + 1]^2} < 1 \tag{II. 12c}$$

for the two values of T defined by $T = T_e$ and

$$T = T_e + (\alpha A / \beta) (\kappa_1 / \kappa_2 + 1)^{-1},$$

$$\frac{[(\kappa_1 / \kappa_2) \exp(\Delta R / T_e) + 1]^2}{(\kappa_1 / \kappa_2) \exp(\Delta R / T_e)} > (\alpha A / \beta) \Delta R / T_e^2 \geq 1. \tag{II. 12d}$$

The last condition, (II. 12d), results from (II. 12b) and (II. 12c). The opposite inequalities are sufficient conditions for uniqueness of the steady state.

D. Occurrence of Hysteresis

The occurrence of multiple steady states suggests the possibility of noncontinuous transitions between these states and hysteresis (Fig. 3). For large enough Δr the system is in a unique steady state A. On decreasing Δr continuously we change the steady state continuously through the points B and C until the tangential point D is reached. A slight additional decrease of Δr results in a discontinuous transition to point F and a further decrease of Δr induces a continuous change to point E, etc. On reversing the process by increasing Δr , we find the system to pass through the points E, F, and G continuously. At the tangential point H a discontinuous jump to point B occurs. The original path is clearly not reproduced, and hysteresis occurs. Points of the type I, where $F'(X) > 1$, are never reached, which suggests that such steady states are unstable. We shall return to this point in Sec. II. E.

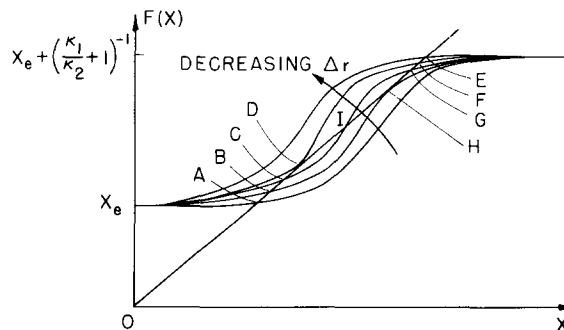


FIG. 3. Multiple steady states and hysteresis resulting for the solution to Eq. (II. 8) for $\Delta r > 0$ (exothermic reaction). The steady state solutions are obtained from the crossing points of the curves $y = X$ and $y = F(X)$.

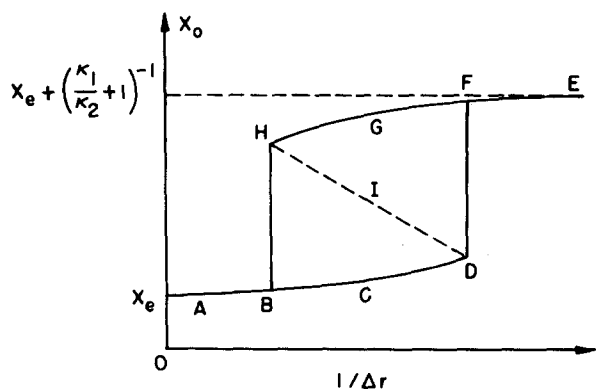


FIG. 4. A schematic description of the hysteresis loop which corresponds to that in Fig. 3. The points A-I correspond to the steady state solutions displayed in Fig. 3. When Δr decreases the system evolves along the ABCDFE path while on a subsequent increase of Δr the path EFGHBA is obtained. The unstable state I is never realized in practice.

A slightly different representation of the hysteresis phenomenon is provided by Fig. 4 where the steady state solution X_0 is plotted schematically as a function of $1/\Delta r$. The path ABCDFE is realized on increasing $1/\Delta r$ while the path EFGHBA occurs on reversing the process. Steady states for which $F'(X_0) > 1$ are located on the line HD which are never realized in practice.

E. Stability of the Steady States

The occurrence of multiple steady states suggests that some of them may be unstable. For our present system we now show that a solution X_0 with $F'(X_0) > 1$ is unstable while solutions which correspond to the opposite inequality are stable.

The stability problem of the steady states is most easily approached by utilizing the Liapounoff theorem¹¹ which states that the conditions for stability of a given steady solution of a nonlinear differential equation are identical to those derived from that equation linearized around the same steady solution. Linearizing the system (II. 3) around a given state solution T_0, A_0 we obtain

$$\frac{d}{dt} \begin{pmatrix} \delta A \\ \delta T \end{pmatrix} = \mathbf{M} \begin{pmatrix} \delta A \\ \delta T \end{pmatrix}, \tag{II. 13}$$

where $\delta A = A - A_0, \delta T = T - T_0$ and, where

$$\mathbf{M} = \begin{pmatrix} -(k_1^0 + k_2^0) & (k_1^0 A_0 / T_0^2) \Delta R \\ \alpha + (k_1^0 + k_2^0) \Delta R / \epsilon & -(\beta + (k_1^0 A_0 / T_0^2) (\Delta R)^2) \end{pmatrix}, \tag{II. 14}$$

in which k_1^0, k_2^0 are the steady-states values of the rate coefficients and ϵ is defined in (II. 4). The characteristic equation is

$$z^2 + bz + c = 0, \tag{II. 15}$$

$$b = \beta + k_1^0 + k_2^0 + (k_1^0 A_0 / \epsilon T_0^2) \Delta R^2,$$

$$c = \beta(k_1^0 + k_2^0) - (\alpha k_1^0 A_0 / T_0^2) \Delta R;$$

one eigenvalue is always negative (as $b > 0$). A necessary and sufficient condition for the other to be positive (and for instability to set in) is $c < 0$ or

$$(\alpha A_0 / T_0^2) \Delta R > \beta [1 + (\kappa_2 / \kappa_1) \exp(-\Delta R / T_0)]$$

which is equivalent to

$$\frac{\alpha \Delta R}{\beta T_0^2} \frac{(\kappa_1 / \kappa_2) \exp(\Delta R / T_0)}{[(\kappa_1 / \kappa_2) \exp(\Delta R / T_0) + 1]^2} > 1. \tag{II. 16}$$

When expressed in the dimensionless variables (II. 16) takes the form

$$F'(X_0) > 1, \tag{II. 17}$$

which provides the proof to the statement that steady states with $F'(X_0) > 1$ are unstable.

Another physical interpretation of this result is obtained by considering variations $\delta A, \delta T$ in which the relation (II. 5a) is maintained, that is the chemical reaction is always at equilibrium at the instantaneous temperature. For such variations Eq. (II. 3b) yields

$$\frac{d\delta T}{dt} = \alpha a \frac{d}{dT} \left[\frac{1}{1 + (\kappa_1 / \kappa_2) \exp(\Delta R / T)} \right]_{T_0} \delta T - \beta \delta T \tag{II. 18}$$

which in the dimensionless representation (II. 7) takes the form

$$d\delta X / dt = \beta [F'(X_0) - 1] \delta X. \tag{II. 19}$$

Again $F'(X_0) > 1$ means instability (δX grows in time). Physically the first term in the rhs of Eq. (II. 18) represents the change in heating rate while the second term represents the change in the heat loss due to the variation δT . For $F'(X_0) > 1$ a small positive change $\delta T > 0$ in the steady-state temperature increases the heating rate more than the cooling rate and thus induces a further increase in the temperature.

F. The Possibility of Oscillations

The linearized Eqs. (II. 13) and (II. 14) of the nonlinear problem provide the condition for oscillatory behavior of fluctuations around the given steady state, $b^2 < 4c$, or

$$[\beta + k_1^0 + k_2^0 + (k_1^0 A_0 / \epsilon T_0^2) \Delta R^2]^2 < 4\beta(k_1^0 + k_2^0) - (4\alpha k_1^0 A_0 / T_0^2) \Delta R. \tag{II. 20}$$

Some simplifications in limiting cases are possible. If for example the term $k_1^0 A_0 / \epsilon T_0^2 (\Delta R^2)$ may be neglected on the lhs (which is reasonable for many systems) relation (II. 20) takes the form

$$(k_1^0 + k_2^0 - \beta)^2 < - (4\alpha k_1^0 A_0 / T_0^2) \Delta R \tag{II. 21}$$

or more explicitly

$$(k_1^0 + k_2^0 - \beta)^2 < - \frac{(4\alpha k_1^0 A_0)}{[T_e + (\alpha/\beta) A_0]^2} \Delta R. \tag{II. 22}$$

It follows from both (II. 20) and (II. 22) that $\alpha \neq 0$ and $\Delta R < 0$ (endothermic reaction $A \rightarrow B$) are necessary conditions for oscillations. This makes it impossible for instability to concur with oscillatory behavior, that is, there cannot be any oscillatory departure from the unstable steady state and any oscillatory behavior is necessarily accompanied by decay. Hence there cannot be any limit cycle in this system. The rhs of inequalities (II. 20) and (II. 22) pass through a maximum as a function of α and go to zero for both $\alpha \rightarrow 0$ and $\alpha \rightarrow \infty$. Oscillations are thus possible only for a limited region of α . If we assume that at the temperature of interest A_0 and k_1^0 are weakly dependent on temperature then this maximum is obtained at the approximate value of α given by $\alpha A_0 = \beta T_e$. From this follows the condition for observing oscillations at some region of α

$$[\beta + k_1^0 + k_2^0 + (k_1^0 A_0 / 4T_e^2)(\Delta R)^2]^2 - 4\beta(k_1^0 + k_2^0) < - (k_1^0 \beta / T_e) \Delta R \quad \text{(II. 23a)}$$

or when (II. 22) is valid

$$(k_1^0 + k_2^0 - \beta)^2 < - (k_1^0 \beta / T_e) \Delta R. \quad \text{(II. 23b)}$$

Physically, when α is too small the system will be too close to equilibrium to exhibit any new features. If α is too large, then the steady state temperature is high and the rate coefficients too insensitive to temperature to maintain the feedback mechanism. The necessity to perform the experiment at low enough temperature will lead us to consider experiments done on transient systems.

G. Transient Experiments

The restrictions imposed on the steady-state temperature, namely its bounding below by the nonequilibrium requirement ($T_0 > T_e$) and above by the requirement that the rate coefficients remain strongly temperature dependent ($T_0 \lesssim \Delta R$), restricts the scope of practical experimental measurements. In order for the reaction to be far enough from equilibrium the rate of light absorption (which corresponds to α) should be at least of the same order of magnitude as the reaction rates [as can be seen from (II. 22)], while in order to obtain a low enough T_0 the cooling process (which corresponds to β) should occur on the same time scale. It is this last condition which is difficult to achieve for moderately fast chemical reactions, as heat conduction in gases and liquids is of limited magnitude.

The scope of the experimental possibilities may be enlarged considerably by looking at systems in nonsteady states. The idea is to take the system out of equilibrium with high intensity light such that the heating rate is of the same order of magnitude as the reaction rate, and to probe its be-

havior during the early stages of its time evolution—far from the high temperature steady state. We take now the uniformly evolving system as our reference state and wish to investigate fluctuations from this time dependent state. As before we linearize the equations but now around the reference state $A_0(t)$ and $T_0(t)$; the nonautonomous linear differential equations for $\delta A(t) = A(t) - A_0(t)$ and $\delta T(t) = T(t) - T_0(t)$ take the form

$$\frac{d}{dt} \begin{pmatrix} \delta A \\ \delta T \end{pmatrix} = \begin{pmatrix} -K(t) & -L(t) \\ \alpha + (\Delta R/\epsilon)K(t) & -\beta + (\Delta R/\epsilon)L(t) \end{pmatrix} \begin{pmatrix} \delta A \\ \delta T \end{pmatrix}, \quad \text{(II. 24)}$$

where

$$K(t) = k_1^0(t) + k_2^0(t) \quad \text{(II. 25a)}$$

and

$$L(t) = [1/T_0(t)^2] [R_1 k_1^0(t) A_0(t) - R_2 k_2^0(t) B_0(t)]. \quad \text{(II. 25b)}$$

A considerable simplification may be achieved if we can assume that at the time of interest the chemical equilibrium concentration relations are not highly perturbed so that approximately $k_1(t)A_0(t) \sim k_2(t)B_0(t)$. With this assumption $L(t)$ takes the simpler form

$$L(t) = - [k_1^0(t)A_0(t) / T_0(t)^2] \Delta R \quad \text{(II. 26)}$$

and we recover Eqs. (II. 13) and (II. 14), only this time with a time dependent matrix \mathbf{M} . If we further assume that on the time scale of interest \mathbf{M} may be regarded as constant, then the approximate behavior of the system in time is obtained as a linear combination of two exponential terms with eigenroots given by the solution of Eq. (II. 15), just as before. As we are now interested particularly in fast reactions we may approximate Eq. (II. 15) by

$$b = k_1^0 + k_2^0 = K, \quad \text{(II. 27)}$$

$$c = - (\alpha k_1^0 A_0 / T_0^2) \Delta R$$

which leads to the condition for oscillatory (stable) modes

$$2\alpha A_0 / T_0 > k(T_0 / \Delta R), \quad \text{(II. 28)}$$

where for simplicity of presentation we took $k_1^0 = k_2^0 = (1/2)K \equiv k$. The validity of the approximation made here, namely the assumption of separation of time scales, may be checked by comparing the time scale for changing the entries of the matrix $\mathbf{M}(t)$, which is approximately $\alpha A_0 / T_0$, with the time scale of an experiment, which is practically the oscillation frequency of the system (around the temporally evolving state).

Taking this frequency to be of the order of $(1/2)c^{1/2}$ we have

$$2\alpha A_0 / T_0 \ll kR / T_0$$

or combining with relation (II. 28)

$$\frac{\Delta R}{T_0(t)} \gg \frac{\alpha A_0(t)/T_0(t)}{k_1^0} \gg \frac{T_0(t)}{\Delta R}. \quad (\text{II. 29})$$

The inequalities (II. 29) provide the validity criterion for observing oscillatory fluctuations in a system evolving in time with frequency much larger than the system's evolution rate, from an initial equilibrium steady state. We note that $\Delta R \sim 10^3$ – 10^4 degrees while $T_0 \sim 10^2$ – 10^3 degrees so that relation (II. 29) may be easily realized in practice. When this is not the case, numerical integration of Eq. (II. 24) is necessary.

H. Systems Involving Intermediates

As a slightly more complicated example which contains an intermediate in the reaction mechanism we treat the system



$$\mathbf{M} = \begin{bmatrix} -(k_1^0 + k_2^0) & -k_2^0 & (k_1^0 A_0 / T_0^2) \epsilon \lambda_1 \\ -k_3^0 & -(k_3^0 + k_4^0) & -(k_4^0 B_0 / T_0^2) \epsilon \lambda_2 \\ \alpha + \lambda_1 (k_1^0 + k_2^0) - \lambda_2 k_3^0 & \lambda_1 k_2^0 - \lambda_2 (k_3^0 + k_4^0) & -[\beta + (\epsilon / T_0^2) (k_1^0 A_0 \lambda_1^2 + k_4^0 B_0 \lambda_2^2)] \end{bmatrix}. \quad (\text{II. 34})$$

From these equations it may be shown that again instability, multiple steady states, and oscillations are possible. A sufficient condition for instability for this problem is

$$\det(\mathbf{M}) > 0 \quad (\text{II. 35})$$

which leads to

$$\alpha (k_1^0 A_0 \epsilon / T_0^2) [(k_3^0 + k_4^0) \lambda_1 + k_3^0 \lambda_2] > \beta (k_1^0 k_2^0 + k_1^0 k_4^0 + k_2^0 k_4^0). \quad (\text{II. 36})$$

Other conditions may be obtained from the general solution of the secular determinant, (II. 35). When k_3 and k_2 go to infinity and R_2 and R_3 go to zero such that k_3/k_2 is kept constant we regain the conditions for the simple $A \rightleftharpoons B$ case with k_1 and k_2 replaced now by $k_1 k_3 / (k_2 + k_3)$ and $k_4 k_2 / (k_2 + k_3)$, respectively (Appendix B). This describes the loss of memory in the C stage: a molecule which leaves the A state does not necessarily go to B, but only with a probability $k_3 / (k_2 + k_3)$. The procedure which takes k_2 and k_3 to infinity does not change the equilibrium constant of the $A \rightleftharpoons C \rightleftharpoons B$ system, which remains $(k_1 k_3) / (k_2 k_4)$. We further note that deviations from the simple $A \rightleftharpoons B$ behavior (of the slowly decaying mode) may be found in the terms of order $1/K$. In principle this deviation may be detected in the experiment considered here and thus may be used for determining the reaction mechanism.

We use all the previous assumptions and define

$$\lambda_1 = (R_2 - R_1) / \epsilon, \quad \lambda_2 = (R_4 - R_3) / \epsilon \quad (\text{II. 31})$$

so that the kinetic equations take the form

$$\begin{aligned} dA/dt &= -k_4 A + k_2 C, \\ dB/dt &= k_3 C - k_4 B, \end{aligned} \quad (\text{II. 32})$$

$$dT/dt = \alpha A - \beta(T - T_e) - \lambda_1 (dA/dt) + \lambda_2 (dB/dt).$$

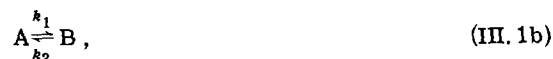
The linearized equations are

$$\frac{d}{dt} \begin{pmatrix} \delta A \\ \delta B \\ \delta T \end{pmatrix} = \mathbf{M} \begin{pmatrix} \delta A \\ \delta B \\ \delta T \end{pmatrix} \quad (\text{II. 33})$$

with

III. THERMODYNAMIC ANALYSIS OF ILLUMINATED REACTIONS

In this section we present a thermodynamic analysis of illuminated reactions. In principle this requires account of photons and consideration of excited species as components. For our purpose, however, it is sufficient to regard the effect of light equivalent to adding a highly energetic chemical species to the system uniformly and at a constant rate. In addition our analysis is simplified by taking a single species A^* to represent the excited A molecule. This approximation is not restrictive when the relaxation process $A^* \rightarrow A$ occurs on a time scale much shorter than the chemical reaction time scale $A \rightarrow B$. Our system may be now described by the following reactions (P stands for light):



where the cycle (III. 1a) is assumed to be far from equilibrium

$$P = \text{constant}; \quad k_3 A P \gg k_{-3} A^*; \quad k_4 A^* \gg k_{-4} A. \quad (\text{III. 2})$$

Also k_3 and k_{-3} are taken to be temperature independent.

Our analysis follows the theory of Glansdorff and Prigogine¹² which is based on Liapounoff's second method for stability analysis.¹³ This approach considers the second variation δ^2s of the local entropy around a steady state as a Liapounoff function. By hypothesis of local equilibrium we have the condition $\delta^2s < 0$ and hence the inequality

$$\partial(\delta^2s)/\partial t > 0 \tag{III. 3}$$

is a sufficient condition for asymptotic stability of the steady state considered. The opposite inequality thus provides indication that instability or at least oscillatory decay to a stable steady state might occur.

For a system with fixed boundary conditions (no diffusion currents and no temperature fluctuation on the boundaries), which is the case for our systems, it has been shown that the local entropy production obeys the equation

$$\frac{1}{2} \partial \delta^2(\rho s) / \partial t = \sum_{\gamma} \delta J_{\gamma} \delta X_{\gamma}, \tag{III. 4}$$

where ρs is the local entropy per unit volume, ρ the constant density, and where J_{γ} and X_{γ} are respectively the flow and its corresponding force for the γ th dissipative process which takes place inside the system. The only flows which have to be considered are chemical (thermal flows are ruled out by the assumption of homogeneity), for which we have

$$J_{\gamma} = T^{-1} \alpha_{\gamma}, \tag{III. 5}$$

where α_{γ} is the chemical affinity for the γ th chemical reaction, defined for ideal mixtures by

$$\alpha_{\gamma}(T) = RT \ln [K_{\gamma}(T) / Q_{\gamma}]. \tag{III. 6}$$

In Eq. (III. 6) K_{γ} is the equilibrium constant of the reactions γ (i. e., the appropriate product of equilibrium concentrations) while Q_{γ} denotes a similar product of the actual chemical concentrations. The stability condition (III. 3) now leads to

$$\sum_{\gamma} \delta [\ln(K_{\gamma} / Q_{\gamma})] \delta v_{\gamma} > 0, \tag{III. 7}$$

where v_{γ} stands for the rate of the γ th reaction.

For comparison we seek first the form which the lhs of relation (III. 7) has for the isolated thermochemical system $A \rightleftharpoons B$. Here

$$\begin{aligned} v_1 &= k_1 A - k_2 B, \\ K_1 / Q_1 &= k_1 A / k_2 B. \end{aligned} \tag{III. 8}$$

and with a straightforward calculation we have (using $\delta A = -\delta B$ and the steady-state relation $k_1 A = k_2 B$)

$$\begin{aligned} &\delta [\ln(K_1 / Q_1)] \delta (k_1 A - k_2 B) \\ &= \left[\left((k_1 + k_2) / \sqrt{k_1 A} \right) \delta A + ((R_1 - R_2) / T_0^2) (k_1 A_0)^{1/2} \delta T \right]^2 \geq 0 \end{aligned} \tag{III. 9}$$

so that this equilibrium system is always stable.

Consider now the contributions to (III. 7) arising from the cycle $A + P \xrightarrow{3} A^* \xrightarrow{4} A$. Invoking the assumption (III. 2) we have

$$\begin{aligned} v_3 &= k_3 AP; \quad K_3 / Q_3 = k_3 AP / k_{-3} A, \\ v_4 &= k_4 A^*; \quad K_4 / Q_4 = k_4 A^* / k_{-4} A \end{aligned} \tag{III. 10}$$

which in turn leads to

$$\begin{aligned} \sum_{r=3}^4 \delta [\ln(K_r / Q_r)] \delta v_r &= k_3 P \delta A (\delta A / A_0 - \delta A^* / A_0^*) \\ &+ [k_4 \delta A^* + (R_4 k_4 A_0^* / T_0^2) \delta T] \\ &\times [\delta A^* / A_0 - \delta A / A_0 + ((R_4 - R_{-4}) / T_0^2) \delta T] \\ &= v (\delta A^* / A_0^* - \delta A / A_0)^2 + (R_4 v / T_0^2) (\delta A^* / A_0^* - \delta A / A_0) \\ &+ [k_4 (R_4 - R_{-4}) / T_0^2] \delta A^* \delta T \\ &+ [v R_4 (R_4 - R_{-4}) / T_0^4] (\delta T)^2. \end{aligned} \tag{III. 11}$$

To obtain this result we have utilized the steady state relation $k_3 P A_0 = k_4 A_0^* \equiv v$. We now introduce the assumption that the photochemical rates v_3, v_4 (III. 10) are much faster than the thermochemical reaction rates $k_1 A, k_2 B$. For the quantities $\langle \delta A \rangle, \langle \delta A^* \rangle$, averaged over a time interval, long on the photochemical time scale yet short on the thermochemical time scale, we have the simple relation $k_3 P \langle \delta A \rangle = k_4 \langle \delta A^* \rangle$ or $\langle \delta A^* \rangle / A_0^* = \langle \delta A \rangle / A_0$. (III. 12)

As we are interested in processes which occur on the thermochemical time scale we may replace, therefore, $\delta A, \delta A^*$ in Eq. (III. 11) by these averages, and utilizing Eq. (III. 12), we obtain

$$\sum_{r=3}^4 \delta [\ln(K_r / Q_r)] \delta v_r = -(R_{-4} k_3 P / T_0^2) \langle \delta A \rangle \delta T, \tag{III. 13}$$

where we have also assumed $R_4 \sim 0$, that is no activation energy is required for the radiationless relaxation processes.

It is seen that the contribution (III. 13) may add a negative term to the stability condition (III. 7) which becomes increasingly important as R_{-4} (the optical excitation energy) and P (the light intensity) become larger. As was demonstrated in Sec. II, this negative contribution may become large enough to interfere with the system's stability. We further note that if B absorbs light in the same spectral region as A (same R_{-4}) with the same efficiency (same k_3) then we have an equivalent contribution to (III. 7) from processes involving B so that the overall contribution of this type becomes

$$(R_{-4} k_3 P / T_0^2) (\langle \delta A \rangle + \langle \delta B \rangle) \delta T = 0 \tag{III. 14}$$

since we have $\langle \delta A \rangle = -\langle \delta B \rangle$.

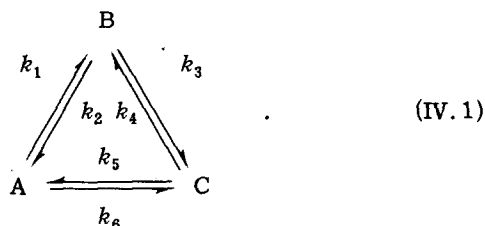
The same conclusion can of course be obtained from the kinetic Eqs. (III. 3). To obtain instability effects the system must be taken out of equilibrium

asymmetrically which is achieved in the present case by adding energy to the system in a way dependent on the density of A only, so that a displacement from chemical equilibrium changes the rate of energy input. This is not the case for the same reaction system heated by, let us say, an electrical resistance heater. The heat input is not coupled to a displacement from the initial chemical equilibrium and no oscillations or instability can occur. A contribution to (III. 9) from heat conduction is always positive.¹⁴

IV. RELAXATION OSCILLATIONS IN A CYCLIC CHEMICAL REACTION SCHEME

In Sec. II we investigated effects of illuminating a chemical system which are due to nonlinear coupling of the rate of a stable reaction mechanism with the rate of change of temperature. We turn now to a different type of interaction of light and chemical reactions, one in which the only function of the light is to displace asymmetrically a reaction mechanisms, by effectively breaking microscopic reversibility. The reaction mechanism itself is sufficiently complex to show oscillatory relaxation upon such displacement.

The possibility of oscillatory phenomena in a cyclic reaction scheme was long ago demonstrated by Hirniak.¹⁰ In what follows we present a modified review of his arguments. Consider the cyclic reaction mechanism given by



The time evolution of this system under isothermal conditions is governed by the following kinetic equation

$$\frac{d}{dt} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} -(k_1 + k_5 + k_6) & k_2 - k_5 \\ k_1 - k_4 & -(k_2 + k_3 + k_4) \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} + \begin{pmatrix} k_5 a \\ k_4 a \end{pmatrix}, \quad (IV. 2)$$

where A, B, C denote species and concentrations while

$$a = A + B + C = \text{const.} \quad (IV. 3)$$

The solution of (IV. 2) is determined by the eigenvalues of the evolution matrix

$$\mathbf{M} \equiv \begin{pmatrix} -(k_1 + k_5 + k_6) & k_2 - k_5 \\ k_1 - k_4 & -(k_2 + k_3 + k_4) \end{pmatrix}, \quad (IV. 4)$$

which are the solutions to the characteristic equation

$$z^2 + bz + c = 0,$$

$$b = \sum_{i=1}^6 k_i, \quad (IV. 5)$$

$$c = (k_1 + k_5 + k_6)(k_2 + k_3 + k_4) - (k_2 - k_5)(k_1 - k_4).$$

The real part of z , $\text{Re}(z)$, is always negative so that stability of the system is insured for any choice of the rate coefficients. However, z may be complex, $\text{Im}(z) \neq 0$, provided that

$$(k_1 + k_5 + k_6 - k_2 - k_3 - k_4)^2 - 4(k_5 - k_2)(k_1 - k_4) < 0 \quad (IV. 6)$$

which implies the necessary condition

$$(k_5 - k_2)(k_1 - k_4) > 0 \quad (IV. 7)$$

for the choice $k_5 > k_2$, $k_1 > k_4$ (i. e., a clockwise direction for the reaction; the opposite choice $k_2 > k_5$; $k_4 > k_1$ leads to an equivalent steady state where the reaction goes in a counterclockwise direction). An additional but not independent condition is $k_3 > k_6$. We now assume that in fact conditions may be established for which

$$\begin{aligned}
 k_1 &\gg k_4, \\
 k_5 &\gg k_2, \\
 k_3 &\gg k_6.
 \end{aligned} \quad (IV. 8)$$

With neglect of the small rate constants, (IV. 6) may be simplified to

$$(k_1 + k_5 - k_3)^2 - 4k_1k_5 < 0. \quad (IV. 9)$$

The frequency of the damped oscillation is

$$\omega = \frac{1}{2} [4k_1k_5 - (k_1 + k_5 - k_3)^2]^{1/2} \quad (IV. 10)$$

while the damping rate is

$$\gamma = \frac{1}{2}(k_1 + k_5 + k_3). \quad (IV. 11)$$

Comparing (IV. 10) and (IV. 11) we see that $\gamma > \omega$ and in most situations the oscillatory behavior will not be amenable to experimental observation due to the large damping rate. However, under the favorable conditions

$$k_1 \sim k_5 \sim \frac{1}{2} k_3 \quad (IV. 12)$$

we have $\gamma \sim 2\omega$ and hence the possibility of observing the effect.

We have thus shown that in principle the system (IV. 1) may under certain conditions show damped oscillations. However, the necessary conditions never exist in equilibrium systems or more generally, in systems which are close to chemical equilibrium. In fact, the necessary conditions

$$k_1 > k_4; \quad k_5 > k_2, \quad k_3 > k_6 \quad (IV. 13)$$

are consistent with the principle of detailed balance,¹⁵ which implies that at equilibrium $k_1A = k_2B$; $k_3B = k_4C$; $k_5C = k_1A$, and which leads to the relation

$$k_1k_3k_5 = k_2k_4k_6, \quad (IV. 14)$$

which is valid at all times. This is clearly contradictory to the conditions (IV. 13). However, in an open system in a nonequilibrium steady state (IV. 13) may be achieved and one way of doing so is by optical excitation. Consider the system (IV. 1) in the presence of light where A may go to B by electronic optical excitation, and B to C by a radiationless relaxation. In that steady state the overall rate constants do not fulfill (IV. 14), and (IV. 13) may be realized. It might be possible to achieve condition (IV. 12) by monitoring the external variables such as light intensity, on which k_1 depends, and pressure of an added inert gas, on which k_5 may depend.

Photochemical systems seem to be practical for observing the predicted oscillations. To achieve the same by chemical means we consider a cycle of the form



where constant flows of D into the system and of E out of the system are applied. This is, of course, equivalent to the photochemical case where light and heat fluxes replace the material flows of D and E, respectively.

Many cyclic reactions of the type (IV. 15) are known¹⁶ which may under favorable experimental conditions exhibit the predicted oscillatory behavior. Moreover, the effects discussed here are not confined to simple triangular mechanism. It may be shown that decaying oscillations may be exhibited by any cyclic mechanism (for a treatment of an equivalent model see Ref. 17) provided that the reaction is maintained far from equilibrium. Material flow or alternatively energy flow are again necessary in order to insure unidirectional reaction evolution (i. e., breaking of detailed balance). Any biochemical cycle thus has the potential ability to oscillate. It should be remembered, however, that in order to obtain sustained oscillations or other types of instabilities, more efficient feedback mechanisms are required.

V. DISCUSSION

We have shown the possibility of damped oscillations, multiple steady states, hysteresis, and instabilities in simple illuminated chemical reactions. In all previous chemical systems the occurrence of such properties required an open system in which mass crossed the boundary of the system, but in our new examples no such mass flows are necessary.

If damped oscillations occur in an illuminated reaction, as discussed in Sec. II., then relaxation experiments yield both a frequency and a decay

rate. In the usual type of relaxation experiment only a decay rate is measured. By applying periodic perturbations we may look for resonance effects in the response, the width of this resonance and its position on the frequency axis are related to the decay rate and to the eigenfrequency of the system. Additional information may be obtained from the relationship between the phases of the perturbation and the response. (For more details see Appendix C). In addition, as was recently proposed,¹⁸ such systems may be probed by light scattering, where the oscillating mode may induce splitting of the scattered Rayleigh band.

Finally it should be noted that other types of systems may be found which exhibit instability and oscillations when maintained asymmetrically far from equilibrium. For example, asymmetrical heating similar to that discussed in the present work may be achieved also by electric current when only one reactant, A say, is ionic and conducts electricity. Such systems are easily analyzed along the lines provided in the present work.

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APPENDIX A: NECESSARY CONDITIONS FOR MULTIPLE STEADY STATES

Here we provide the proof for Eqs. (II. 12). By inspection of Fig. 2 the two first conditions (II. 12 a, b) become obvious. Condition (II. 12c) is obtained from the observation (Fig. 2) that in order for multiple steady states to occur the slope of the function $F(X)$ must be smaller than 1 for both $X = X_e$ and $X = X_e + 1/[(\kappa_1 + \kappa_2) + 1]$. Transforming back to the original variables we obtain (II. 12c), which is identical to the left inequality of (II. 12d). The right inequality of (II. 12d) is just a necessary condition for condition (II. 12b) to be held, as may be seen from the expression for $F'(X)$, Eq. (II. 10).

APPENDIX B: A DISCUSSION OF THE $A \rightleftharpoons C \rightleftharpoons B$ SYSTEM IN THE LIMIT OF FAST $A \leftarrow C \rightarrow B$ REACTIONS

Starting from Eqs. (II. 30)–(II. 34) we want to obtain the roots of the matrix \mathbf{M} in the limit $k_2^0, k_3^0 \rightarrow \infty, R_2, R_3 \rightarrow 0$ provided that $k_2^0/k_3^0 = \text{const}$. Physically it is expected that this limit will correspond to the simple $A \rightleftharpoons B$ scheme. Defining $k_2^0 = Kk_2^{0'}$, $k_3^0 = Kk_3^{0'}$, with $k_2^{0'}$, $k_3^{0'}$ finite and $K \rightarrow \infty$, the characteristic equation for the roots of \mathbf{M} is obtained in the form

$$\begin{aligned} z^3 &+ [K(k_2^{0'} + k_3^{0'}) + k_1^0 + k_4^0 + M_3]z^2 + \{K[k_2^{0'}k_4^0 \\ &+ k_1^0k_3^{0'} + (k_2^{0'} + k_3^{0'})M_3 + (\lambda_1k_2^{0'} - \lambda_2k_3^{0'})M_1 + M_2]\} \\ &+ k_1^0k_4^0 + (k_1^0 + k_4^0)M_3 + M_1\alpha + \lambda_1k_1^0M_1 - \lambda_2k_4^0M_2\}z \end{aligned}$$

$$+K[\beta(k_1^{0'}k_3^{0'} + k_2^{0'}k_4^{0'}) - \alpha(k_2^{0'}M_2 - k_3^{0'}M_1)] \\ + \alpha k_4^0 M_3 + \beta k_1^0 k_4^0 = 0, \quad (\text{B1})$$

where we have defined

$$M_1 = - (k_1^0 A_0 / T_0^2) \epsilon \lambda_1; \quad M_2 = + (k_4^0 B_0 / T_0^2) \epsilon \lambda_2 \\ M_3 = + [\beta + (\epsilon / T_0^2) (k_1^0 A_0 \lambda_1^2 + k_4^0 B_0 \lambda_2^2)]. \quad (\text{B2})$$

The desired roots are now expanded in the form

$$z = z_1 K + z_0 + z_{-1} / K + \dots, \quad (\text{B3})$$

and terms with equal powers of K are considered.

From the terms of order K^3 we obtain

$$z_1^3 + (k_2^{0'} + k_3^{0'}) z_1^2 = 0 \quad (\text{B4})$$

from which we get

$$z_1^{(1,2)} = 0, \\ z_1^{(3)} = - (k_2^{0'} + k_3^{0'}). \quad (\text{B5})$$

The root $z_1^{(3)}$ represents a rapidly decaying mode which arises from the fast reactions $A \rightarrow C \rightarrow B$. We are interested in such roots for which $z_1 = 0$. From these roots we obtain from terms of order K the equation for $z_0^{(1,2)}$

$$(k_2^{0'} + k_3^{0'}) z_0^2 + [k_2^{0'} k_4^{0'} + k_1^0 k_3^{0'} + (k_2^{0'} + k_3^{0'}) M_3 \\ + (\lambda_1 k_2^{0'} \lambda_2 k_3^{0'}) (M_1 + M_2)] z_0 + \beta (k_1^0 k_3^{0'} + k_2^{0'} k_4^0) \\ - \alpha (k_2^{0'} M_2 - k_3^{0'} M_1) = 0. \quad (\text{B6})$$

Utilizing now the relations

$$\lambda_1 = -R_1 / \epsilon; \quad \lambda_2 = R_4 / \epsilon, \\ k_1 A_0 = k_4 B_0 (k_2 / k_3) = k_2 C_0 \quad (\text{B7})$$

we transform (B6) into the form

$$X_0^2 + [\bar{k}_1^0 + \bar{k}_4^0 + \beta + (\bar{k}_1 A_0 / \epsilon T_0^2) (R_1 - R_4)^2] + \beta (\bar{k}_1^0 + \bar{k}_4^0) \\ - (\alpha \bar{k}_1 A_0 / T_0^2) (R_1 - R_4) \quad (\text{B8})$$

with

$$\bar{k}_1^0 = k_1^0 k_3 / (k_2 + k_3); \quad \bar{k}_4^0 = k_4^0 k_2 / (k_2 + k_3). \quad (\text{B9})$$

Comparing (B8) to (II. 15) we see that indeed we regain the result for the simple $A \rightleftharpoons B$ scheme with rate coefficients modified according to Eq. (B9).

APPENDIX C: RESONANCE RESPONSE TO PERIODIC PERTURBATION

Let us consider the change in the model experiment, Sec. II.A, for which we add to the steady illumination, proportional to α in (II. 3b), a periodic

term

$$\alpha + \alpha' \cos \omega' t; \quad \alpha' \ll \alpha. \quad (\text{C1})$$

The homogeneous Eq. (II. 13) is now replaced by the inhomogeneous equation

$$\frac{d}{dt} \begin{pmatrix} \delta A \\ \delta T \end{pmatrix} = \mathbf{M} \begin{pmatrix} \delta A \\ \delta T \end{pmatrix} + \begin{pmatrix} 0 \\ A_0 \alpha' \cos \omega' t \end{pmatrix}, \quad (\text{C2})$$

where \mathbf{M} is given by Eq. (II. 14).

Focusing our attention on the case where relaxation oscillations are exhibited in the homogeneous case, we are interested in the nonhomogeneous part of the solution to Eq. (C2) (the homogeneous part decays to zero in time). This is proportional to the function

$$f(\omega') = \cos(\omega' t - \phi) / [(r^2 + \omega^2 - \omega'^2)^2 + 4r^2 \omega'^2]^{1/2}, \quad (\text{C3})$$

where $r \pm i\omega$ are the eigenvalues of the matrix \mathbf{M} , and where

$$\phi = \arctan(2r\omega' / (r^2 + \omega^2 - \omega'^2)), \quad (\text{C4})$$

which shows typical resonance behavior.

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