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STABILITY OF PHOTOCHEMICAL MECHANISMS FOR PHOTO-GALVANIC CELLS

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Summary

A general analysis of the stability properties of photochemical mechanisms for photogalvanic cells is presented. We consider a model, recently introduced, for photoredox systems in which a one-electron redox couple (here an inorganic couple) reacts with a two-electron redox couple (here an organic dye). We consider first the case of a well-stirred cell. A linear stability analysis and then a thermodynamic stability analysis are carried out for each of six possible mechanisms allowed by the model; similar analyses are performed to determine the stability at certain coordinates of the kinetic "phase diagram" where two (or more) mechanisms may compete. Taken together, the results of these analyses indicate that the photostationary state is asymptotically stable in all the kinetic regimes investigated. We next study how these conclusions are changed when diffusion of the reactants is taken into account explicitly. The general analysis is then specialized to treat a particular well-known photogalvanic cell, the iron–thionine system. The identity and the stability of the photostationary state for this system are investigated and are then quantified as functions of the concentration of the metal ion Fe^{3+} and the system illumination. Our results on this specific photogalvanic system are examined in the light of known results on the stability properties of coupled chemical networks and are correlated with a recent study of the optimum efficiency of photogalvanic cells for solar energy conversion.

1. Introduction

Recently Albery *et al.* [1] have presented a study of the possible mechanisms for a certain class of photoredox systems in which a one-electron redox couple reacts with a two-electron redox couple. The system chosen for study was designed to model a common type of photogalvanic cell which employs an organic dye redox couple (such as thionine) and an inorganic redox couple (such as Fe(II), Fe(III)). The organic redox couple involves two electrons and the chemical problem is formulated as a two-step process:

$$A + e \; \rightleftarrows \; B \tag{1a}$$

$$B + e \; \rightleftarrows \; C \tag{1b}$$

where protonation is ignored; if the species A is thionine, then B is the semithionine radical and C is (doubly-reduced) leucothionine. If Fe(II) is designated as Z and Fe(III) as Y, the inorganic couple is written as
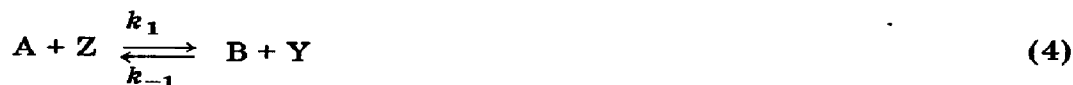
$$Y + e \; \rightleftarrows \; Z \tag{2}$$

Experimentally it is found that in the absence of illumination the equilibrium between the two couples is very much in favor of thionine (A) and Fe^{2+} (Z), whereas under illumination a new photostationary state is established with significant production of leucothionine (C) and Fe^{3+} (Y):

$$A + 2Z \; \xrightarrow{h\nu} \; C + 2Y \tag{3}$$

The products C and Y then react on the electrodes in a photogalvanic cell to produce power. Albery *et al.* [1] demonstrate that there are six possible mechanisms by which the system described by eqns. (1) - (3) can react, with the mechanism actually realized being dependent on the concentrations of the individual species, the rate constants and the irradiance of the light. They present a mechanistic "phase diagram" wherein the interrelationship of the six possible mechanisms is clearly displayed and they comment on the general implications of their study for photogalvanic cells. In a subsequent contribution Albery *et al.* [2] go on to show how the analysis presented in ref. 1 allows the actual mechanism of the iron–thionine photoredox system to be determined. Depending on the experimental conditions they find that this one-electron–two-electron system can react by two of the six possible mechanisms identified in ref. 1. With these results they are able to comment on the optimal conditions for the conversion of solar energy into electrical energy for the iron–thionine system.

The purpose of the present study is to address the important question of dynamic stability of the general photoredox scheme described by eqns. (1) - (3), both in the regime where one mechanism dominates and at those coordinates of the mechanistic "phase diagram" where two (or more) of the six possible mechanisms may play a role. We shall consider first the case where the reactants in the cell may be assumed to be "well stirred" and then take up the more realistic case where diffusion of the reactants is taken into account explicitly.

Following the notation of ref. 1 we consider the thermal reactions

$$A + Z \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; B + Y \tag{4}$$

$$B + Z \; \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \; C + Y \tag{5}$$

$$B + B \xrightarrow[\substack{k_{-3}}]{\substack{k_3}} A + C \qquad (6)$$

and assign a flux g to the photochemical reaction

$$A + Z \xrightarrow{h\nu} B + Y \qquad (7)$$

where

$$g = \phi_B I\epsilon [A] \equiv \tilde{g} [A] \qquad (8)$$

Here, for monochromatic radiation ϕ_B is the quantum efficiency for the production of B from A and Z, I is the irradiance of the monochromatic light and ϵ is the molar extinction coefficient of A; in this study we shall regard the product $\phi_B I\epsilon \equiv \tilde{g}$ to be a constant, although such a restriction can be removed easily if warranted experimentally. For a photogalvanic system, closed with respect to mass transport, the problem defined by eqns. (4) - (7) has the following kinetic description:

$$\frac{\partial [A]}{\partial t} = D_A \nabla^2 [A] - g + k_{-1} [B] [Y] + k_3 [B]^2 - k_{-3} [A] [C] \qquad (9)$$

$$\frac{\partial [B]}{\partial t} = D_B \nabla^2 [B] + g - k_{-1}[B] [Y] - k_2[B] [Z] + k_{-2}[C] [Y] -$$

$$- 2k_3 [B]^2 + 2k_{-3} [A] [C] \qquad (10)$$

$$\frac{\partial [C]}{\partial t} = D_C \nabla^2 [C] + k_2[B] [Z] - k_{-2}[C] [Y] + k_3[B]^2 -$$

$$- k_{-3} [A] [C] \qquad (11)$$

$$\frac{\partial [Z]}{\partial t} = D_Z \nabla^2 [Z] - g + k_{-1}[B] [Y] - k_2[B] [Z] + k_{-2}[C] [Y] \qquad (12)$$

$$\frac{\partial [Y]}{\partial t} = D_Y \nabla^2 [Y] + g - k_{-1}[B] [Y] + k_2[B] [Z] - k_{-2}[C] [Y] \qquad (13)$$

It is evident that eqns. (9) - (13) are coupled and are non-linear; in analyzing these equations it will be assumed that the system is isothermal and that no further non-linearities are brought into the problem through the rates k_i and k_{-i}; this important point will be discussed in the concluding section.

In the following section we present the results of a linear stability analysis for the system described by eqns. (9) - (13) in the case where the diffusion terms are suppressed (the well-stirred case) for each of the six possible kinetic regimes identified in ref. 1. A representative calculation is

carried through in detail for two of the possibilities and the final results for the remaining cases are noted. The behavior of the system at a mechanistic "phase boundary" is also considered in Section 2, a representative calculation is presented and our results are summarized. The section concludes with a (Glansdorff–Prigogine) thermodynamic stability analysis of the well-stirred case and the results obtained are shown to complement those found via the linear stability analysis. In Section 3 we consider the role of reactant diffusion in influencing the predictions of the stability analyses presented in Section 2. Then in Section 4 we apply both linear stability analysis and thermodynamic stability analysis to the specific photogalvanic system studied by Albery *et al.* [2], *i.e.* the iron–thionine system. The implications of our analysis in assessing the stability of photogalvanic systems involving an organic dye redox couple and an inorganic redox couple are discussed in the concluding section.

2. Stability analysis of a well-stirred photogalvanic cell

2.1. Linear stability analysis

We consider first the case where the cell is closed with respect to mass transport and all effects due to diffusional flows of reactants are suppressed. Given these two constraints on the mass flux the following conservation conditions can be verified easily:

$$[A] + [B] + [C] = [A]_i + [B]_i + [C]_i \equiv a \tag{14}$$

$$[Y] + [Z] = [Y]_i + [Z]_i \equiv b \tag{15}$$

$$[Z] + [C] - [A] = [Z]_i + [C]_i - [A]_i \equiv d \tag{16}$$

where the subscript i denotes the initial concentration of the particular species and where $\{a, b, d\}$ are constants. Hence the overall reaction–diffusion system collapses to the following pair of dynamic equations:

$$\frac{d[A]}{dt} = -\widetilde{g}\,[A] + k_{-1}[B][Y] + k_3[B]^2 - k_{-3}[A][C] \tag{17a}$$

$$= -\widetilde{g}\,[A] + k_{-1}(a - [A] - [C])(b - d - [A] + [C]) +$$

$$+ k_3(a - [A] - [C])^2 - k_{-3}[A][C] \tag{17b}$$

$$\equiv P \tag{17c}$$

and

$$\frac{d[C]}{dt} = k_2[B][Z] - k_{-2}[C][Y] + k_3[B]^2 - k_{-3}[A][C] \tag{18a}$$

$$= k_2(a - [A] - [C])(d + [A] - [C]) - k_{-2}[C](b - d - [A] +$$

$$+ [C]) + k_3(a - [A] - [C])^2 - k_{-3}[A][C] \qquad (18b)$$

$$\equiv Q \qquad (18c)$$

The general problem of characterizing the stability of a non-equilibrium state, relative to some reference state, by determining and then classifying the singular points of the differential equations defining the system under study has been discussed in detail in a number of recent articles and monographs (see for example ref. 3). For that reason we do not review here the background of the method, but simply remark that the stability of a given photostationary state in the present problem can be determined by computing the eigenvalues of the characteristic equation associated with the linear system:

$$\frac{d(\delta[A])}{dt} = P_A(\delta[A]) + P_C(\delta[C]) \qquad (19a)$$

$$\frac{d(\delta[C])}{dt} = Q_A(\delta[A]) + Q_C(\delta[C]) \qquad (19b)$$

Here the subscripts on P and Q denote differentiation with respect to the variables [A] and [C]. Specifically, we must solve the algebraic equation

$$s^2 - (P_A + Q_C)s + (P_A Q_C - P_C Q_A[A]) = 0 \qquad (20)$$

where

$$P_A = -\tilde{g} - k_{-1}(b - d - [A] + [C]) - k_{-1}(a - [A] - [C]) -$$

$$- 2k_3(a - [A] - [C]) - k_{-3}[C] \qquad (21a)$$

$$P_C = -k_{-1}(b - d - [A] + [C]) + k_{-1}(a - [A] - [C]) -$$

$$- 2k_3(a - [A] - [C]) - k_{-3}[A] \qquad (21b)$$

$$Q_A = k_2(a - [A] - [C]) - k_2(d + [A] - [C]) + k_{-2}[C] -$$

$$- 2k_3(a - [A] - [C]) - k_{-3}[C] \qquad (21c)$$

$$Q_C = -k_2(a - [A] - [C]) - k_2(d + [A] - [C]) -$$

$$- k_{-2}(b - d - [A] + [C]) - k_{-2}[C] - 2k_3(a - [A] - [C]) -$$

$$- k_{-3}[A] \qquad (21d)$$

and where the derivatives are evaluated using the steady state values $\{[A]_0, [B]_0, [C]_0\}$ of the several concentration variables appearing in eqns. (21). In order to avoid too cumbersome a notation, in this section we shall drop

the subscripts on the values $\{[A]_0, [B]_0, [C]_0\}$ and use unsubscripted variables to denote the reference state concentrations. Depending on whether the eigenvalues $s = s_1, s_2$ so determined are real or complex, positive or negative, different conclusions regarding the stability of a given photostationary state are possible. To investigate the stability of the possible photostationary states that can arise in the system eqns. (1) - (3) (in effect, to study the dynamical stability of systems governed by one of the six mechanisms identified by Albery *et al.* [1]), we use the conservation conditions eqns. (14) - (16) to recast eqns. (21) in terms of the organic dye variables $\{[A], [B], [C]\}$ and the metal ion concentrations $\{[Y], [Z]\}$, and we then write

$$P_A = -\tilde{g} - k_{-1}([Y] + [B]) - 2k_3[B] - k_{-3}[C] \tag{22a}$$

$$P_C = -k_{-1}([Y] - [B]) - 2k_3[B] - k_{-3}[A] \tag{22b}$$

$$Q_A = k_2([B] - [Z]) + k_{-2}[C] - 2k_3[B] - k_{-3}[C] \tag{23a}$$

$$Q_C = -k_2([B] + [Z]) - k_{-2}([Y] + [C]) - 2k_3[B] - k_{-3}[A] \tag{23b}$$

From the theory of quadratic equations we have at once that

$$s_1 + s_2 = P_A + Q_C$$

$$= -\tilde{g} - k_{-1}[Y] - 4k_3[B] - k_{-3}[C] - k_{-1}[B] -$$

$$- k_2[Z] - k_{-2}[Y] - k_{-3}[A] - k_2[B] - k_{-2}[C] \tag{24a}$$

and

$$s_1 s_2 = P_A Q_C - P_C Q_A$$

$$= (-\tilde{g} - k_{-1}[Y] - 2k_3[B] - k_{-3}[C] - k_{-1}[B]) \times$$

$$\times (-k_2[Z] - k_{-2}[Y] - 2k_3[B] - k_{-3}[A] - k_2[B] - k_{-2}[C]) -$$

$$- (-k_{-1}[Y] - 2k_3[B] - k_{-3}[A] + k_{-1}[B]) \times$$

$$\times (-k_2[Z] + k_{-2}[C] - 2k_3[B] - k_{-3}[C] + k_2[B]) \tag{24b}$$

Given that the various factors (concentrations and rate constants) appearing in eqns. (24) are inherently positive quantities and since $s_1 + s_2 \leqslant 0$, it is clear that either we must have two real roots, one or both of which may be negative (depending on the sign of the product $s_1 s_2$), or s_1 and s_2 are complex conjugates. If both $\mathrm{Re}\, s_i < 0$ ($i = 1$ or 2), the associated photostationary state is asymptotically stable. If, however, $s_1 s_2 < 0$, then one eigenvalue will be negative and the other will be positive; $\mathrm{Re}\, s_i > 0$ ($i = 1$ or 2) implies that the associated photostationary state will be unstable (say to perturbations or fluctuations).

The question formulated in Section 1 can now be posed clearly. For each of the six possible mechanisms identified by Albery *et al.* [1] in their general treatment of photochemical mechanisms for photogalvanic cells, we determine which (if any) of these mechanisms results in a photostationary state which is asymptotically stable. As promised in Section 1, we shall carry through the analysis explicitly for two representative mechanisms and shall simply record the results for the remaining mechanisms. Following this, we shall take up the important question of stability/instability at a mechanistic "phase boundary". Before proceeding, however, we note that for a system closed with respect to mass transport (the present section) only one set of steady state concentrations is consistent with the dual constraints that the individual concentrations must be positive and that their composite sum must be bounded from above by the value a.

The six possible mechanisms identified in ref. 1 emerge on examining the structure of the general steady state condition and are defined by certain inequalities relating concentrations and rate constants. These inequalities are

$$k_{-1}[B][Y] > \frac{k_{-2}k_3[B]^2[Y]}{k_{-2}[Y] + k_{-3}[A]} \tag{25}$$

$$k_2[Z] > k_3[B] \tag{26}$$

$$k_{-2}[Y] > k_{-3}[A] \tag{27}$$

The condition eqn. (25) is referred to in ref. 1 as A1, eqn. (26) is B1 and eqn. (27) is C1, with the reverse of these inequalities being designated as A2, B2 and C2 respectively. The overall mechanism is a combination of one of each of the pairs A1 or A2, B1 or B2 and C1 or C2. Of the eight possible combinations, only six are self-consistent and these are A1 B1 C1, A1 B2 C1, A1 B2 C2, A2 B1 C1, A2 B2 C1 and A2 B2 C2. Having identified these possibilities Albery *et al.* [2] show that two of the mechanisms, A1 B2 C1 and A2 B2 C1, may be realized in the iron–thionine system (depending on the experimental conditions) with the optimum production of leucothionine being achieved in the regime where the mechanism A2 B2 C1 pertains. Accordingly we choose these mechanisms to illustrate the details of the stability analysis.

The basic task is to determine the algebraic sign of the product $s_1 s_2$. Among the terms generated on expanding the products in eqn. (24b), only four negative terms are found, *i.e.* $k_{-1}[B]k_2[B]$, $k_{-1}[B]k_{-2}[C]$, $k_{-1}[Y]k_{-3}[C]$ and $k_{-3}[A]k_2[Z]$; our program then is to assess the importance of these negative terms relative to the positive terms. To proceed we may first of all take advantage of the fact that in most photogalvanic cells the concentrations of the inorganic couple Y,Z are much larger than the concentrations of the organic dye (see the discussion in ref. 1). Accordingly we group certain negative terms generated in the expansion of eqn. (24b) ($k_{-1}[B]k_2[B]$ and $k_{-1}[B]k_{-2}[C]$) with positive terms (respectively $k_2[B]k_{-1}[Y]$ and $k_{-1}[B]k_{-2}[Y]$) in such a way that the overall contribution to $s_1 s_2$ is positive, *i.e.* we notice

$$k_2[B] k_{-1}[Y] - k_{-1}[B] k_2[B] = k_2[B] k_{-1}([Y] - [B]) > 0 \qquad (28)$$

and

$$k_{-1}[B] k_{-2}[Y] - k_{-1}[B] k_{-2}[C] = k_{-1}[B] k_{-2}([Y] - [C]) > 0 \quad (29)$$

Again the inequalities hold since experimentally $[Y] \gg [B], [C]$. Also, the experimental conditions are such [1] that

$$\frac{k_2 k_{-3}[A][Z]}{k_{-2} k_3[Y][B]} \ll 1$$

so in eqn. (24b) we are guaranteed

$$2k_3 k_{-2}[B][Y] - k_2 k_{-3}[A][Z] > 0 \qquad (30)$$

So, what it comes down to is that, of the four possible negative terms in the expression for $s_1 s_2$, three of these ($k_{-1}[B] k_2[B]$, $k_{-1}[B] k_{-2}[C]$ and $k_3[A] k_2[Z]$) can be coupled with positive terms in such a way that the overall contribution to the product $s_1 s_2$ is positive. To establish conclusively the sign of $s_1 s_2$, it is only necessary to assess the importance of the single remaining negative term $k_{-1}[Y] k_{-3}[C]$ in each of the possible mechanisms. For definiteness let us consider the mechanism A1 B2 C1; using the constraints implied in the specification A1, B2, C1 (see the discussion immediately following eqns. (25) - (27)), the rate equations at the steady state may be simplified to read

$$\frac{d[A]}{dt} = - \tilde{g}[A] + k_{-1}[B][Y] = 0$$

$$\frac{d[C]}{dt} = - k_{-2}[C][Y] + k_3[B]^2 = 0$$

From the first of these equations we have

$$\tilde{g} k_3[B] = k_{-1}[Y] \frac{k_3[B]^2}{[A]}$$

and from the second equation we have

$$k_3[B]^2 = k_{-2}[C][Y]$$

Now, from the condition C1

$$k_{-2}[Y] > k_{-3}[A]$$

we have

$$\tilde{g} k_3[B] = k_{-1}[Y] \frac{k_3[B]^2}{[A]} = k_{-1}[Y] \frac{k_{-2}[C][Y]}{[A]}$$

$$> k_{-1}[Y] \frac{[C]}{[A]} k_{-3}[A] = k_{-1}[Y] k_{-3}[C]$$

Hence the final couple the sign of which must be determined to specify the overall sign of the product $s_1 s_2$ is

$$\tilde{g} k_3[B] - k_{-1}[Y] k_{-3}[C] > 0 \tag{31}$$

This last result completes the specification of $s_1 s_2$. We are guaranteed that $s_1 s_2$ is positive for the mechanism A1 B2 C1. In turn, this means that the two eigenvalues s_1 and s_2 are negative, *i.e.* that the photostationary state realized when the mechanism A1 B2 C1 is operative is an asymptotically stable non-equilibrium steady state.

As a second example let us consider the mechanism A2 B2 C1. Using the constraints specified by the inequalities B1 and C1, the rate equation for the component C at the steady state is simplified to

$$\frac{d[C]}{dt} = k_3[B]^2 - k_{-2}[C][Y] = 0$$

from which we determine

$$k_3[B]^2 = k_{-2}[C][Y]$$

According to the condition C1

$$k_{-2}[Y] > k_{-3}[A]$$

we have

$$k_3[B]^2 = k_{-2}[C][Y] > k_{-3}[A][C]$$

Also, from the conditions A2 and C1 we have

$$k_{-1}[B][Y] < \frac{k_{-2}k_3[B]^2[Y]}{k_{-2}[Y] + k_{-3}[A]}$$

$$\approx k_3[B]^2$$

Now, using these two inequalities the rate equation for component A at the steady state is simplified to

$$\frac{d[A]}{dt} = -\tilde{g}[A] + k_3[B]^2 = 0$$

so that

$$\tilde{g} = \frac{k_3[B]^2}{[A]} = \frac{k_{-2}[C][Y]}{[A]}$$

Again, considering the condition C1, we may specify

$$\tilde{g} = \frac{k_{-2}[C][Y]}{[A]} > k_{-3}[C]$$

So finally, using the condition A2, *i.e.*

$$k_{-3}[B] > k_{-1}[Y]$$

we are guaranteed

$$\tilde{g} k_{-3}[B] - k_{-3}[C] k_{-1}[Y] > 0 \tag{32}$$

and we have proved that the product $s_1 s_2$ is positive. That is, once again the eigenvalues s_1 and s_2 are negative and the photostationary state is asymptotically stable. In fact, analyses exactly similar to those performed for the mechanisms A1 B2 C1 and A2 B2 C1 show that the photostationary state realized for each of the six possible mechanisms is asymptotically stable.

To conclude this subsection we consider the stability of the photostationary state at coordinates of the mechanistic "phase diagram" which constitute "phase boundaries" between mechanisms. Once again we illustrate the method using a single example and we simply state the final results for the other possibilities. As our single example we recall again the result of ref. 2 that, depending on whether k_{-2} or $k_{-1}(k_{-2}[Y]/k_3[C])^{1/2}$ is dominant, the mechanism for the iron–thionine system will be either A2 B2 C1 or A1 B2 C1 respectively. The sense of the constraints B2 and C1 is as before (see the discussion following eqns. (25) - (27)); accordingly, using the inequalities B2 and C1 the rate equation for component C at the steady state simplifies to

$$\frac{d[C]}{dt} = k_3[B]^2 - k_{-2}[C][Y] = 0$$

so that

$$k_3[B]^2 = k_{-2}[C][Y]$$

and from the condition C1 we have

$$k_{-2}[C][Y] > k_{-3}[A][C]$$

Now, according to the constraint A1 = A2 and the condition C1, we have

$$k_{-1}[Y] = k_3[B]$$

Thus

$$k_{-1}[B][Y] = k_3[B]^2 = k_{-2}[C][Y] > k_{-3}[A][C]$$

With these results the rate equation for component A at the steady state may be written as

$$\frac{d[A]}{dt} = -\tilde{g}[A] + 2k_3[B]^2 = 0$$

so that

$$\tilde{g} = \frac{2k_3[B]^2}{[A]} = \frac{2k_{-2}[C][Y]}{[A]}$$

Using the condition C1 we find

$$\frac{k_{-2}[Y]}{[A]} > k_{-3}$$

so that

$$\tilde{g} = \frac{2k_{-2}[C][Y]}{[A]} > 2k_{-3}[C]$$

Thus

$$\tilde{g}\,k_3[B] > 2k_{-3}[C]\,k_{-1}[Y]$$

and once again

$$\tilde{g}\,k_3[B] - k_{-3}[C]\,k_{-1}[Y] > 0 \tag{33}$$

which guarantees that the product $s_1 s_2$ is positive. As noted earlier, we may then conclude that s_1 and s_2 are negative thereby guaranteeing the asymptotic stability of the associated photostationary state. In fact, exactly this conclusion is obtained at all the mechanistic "phase boundaries" except those for which B1 = B2 and C1 = C2 hold simultaneously. Mechanisms for which these latter constraints pertain (simultaneously) are not possible since here it can be shown that

$$\frac{k_2 k_{-3}[A][Z]}{k_{-2} k_3[Y][B]} = 1$$

whereas on experimental grounds [1] it is known that this ratio must be significantly smaller than unity.

2.2. Thermodynamic stability analysis

The results of the linear stability analysis presented in Section 2.1 can be complemented with those obtained in a thermodynamic stability analysis of the photogalvanic model, eqns. (1) - (3), which was introduced in ref. 1 and is studied further in this work. Here the theory of Glansdorff and Prigogine [4] will be implemented. In this theory we imagine a system to be perturbed from a given steady state, and we consider the second variation of the local entropy $\delta^2 S$ around this steady state. Treating $\delta^2 S$ as a Liapunoff function and using the hypothesis of local equilibrium, it is shown in ref. 4 that $\delta^2 S \leqslant 0$ and

$$\frac{\partial(\delta^2 S)}{\partial t} > 0 \tag{34}$$

where the second inequality is a sufficient condition for the asymptotic stability of the steady state. If the reverse of inequality (34) is satisfied, this is an indication that instability or at least oscillatory decay to a stable steady state may occur.

Considering the entropy production in a system with fixed boundary conditions, it is found that

$$\frac{1}{2}\frac{\partial(\delta^2 S)}{\partial t} = \sum_{\gamma}\delta J_{\gamma}\delta X_{\gamma}$$

where J_{γ} and X_{γ} are respectively the flow and driving force characterizing the γth dissipative process inside the system. Consider now an isothermal and spatially homogeneous system consisting of a number of chemically reacting species distributed in an inert solvent. The flow J_{γ} may be identified as the reaction rate r_{γ} of the γth reaction, with the driving force X_{γ} of that reaction expressed by

$$X_{\gamma} = \frac{1}{T}a_{\gamma} = R\ln\left(\frac{K_{\gamma}}{Q_{\gamma}}\right)$$

In this last relation a_{γ} is the chemical affinity for the γth chemical reaction, K_{γ} and Q_{γ} are the appropriate products of equilibrium versus actual chemical concentrations respectively in the reacting system, R is the universal gas constant and T is the (constant) temperature of the system. In these notations the formal stability condition (34) may be expressed as

$$\sum_{\gamma}\delta\ln\left(\frac{K_{\gamma}}{Q_{\gamma}}\right)\delta r_{\gamma} > 0 \tag{35}$$

In the photogalvanic system considered in this work, we have

$$\frac{K_1}{Q_1} = \frac{\tilde{g}[A]}{k_{-1}[B][Y]} \qquad r_1 = \tilde{g}[A] - k_{-1}[B][Y] \tag{36a}$$

$$\frac{K_2}{Q_2} = \frac{k_2[B][Z]}{k_{-2}[C][Y]} \qquad r_2 = k_2[B][Z] - k_{-2}[C][Y] \tag{36b}$$

$$\frac{K_3}{Q_3} = \frac{k_3[B]^2}{k_{-3}[A][C]} \qquad r_3 = k_3[B]^2 - k_3[A][C] \tag{36c}$$

Given the earlier conservation conditions (14) - (16), we note that

$$\delta[B] = -\delta[A] - \delta[C] \tag{37a}$$

$$\delta[Y] = -\delta[Z] \tag{37b}$$

$$\delta[Z] = \delta[A] - \delta[C] \tag{37c}$$

Using these equations (and recalling that from our earlier discussion $1/[Y]$, $1/[Z] \ll 1/[A]$, $1/[B]$, $1/[C]$ in this system), the formal relation (35) can be written

$$\frac{1}{2R}\frac{\partial(\delta^2 S)}{\partial t} = \left\{\delta[A]\left(\frac{1}{[A]_0}+\frac{1}{[B]_0}\right)+\delta[C]\frac{1}{[B]_0}\right\}\left\{\delta[A](\tilde{g}+\right.$$

$$\left.+k_{-1}[Y])+\delta[C](k_{-1}[Y])\right\}+\left\{\delta[A]\left(-\frac{1}{[B]_0}\right)+\right.$$

$$\left.+\delta[C]\left(-\frac{1}{[B]_0}-\frac{1}{[C]_0}\right)\right\}\left\{\delta[A](-k_2[Z]+\right.$$

$$\left.+k_{-2}[C]_0\ (+\delta[C](-k_2[Z]-k_{-2}[Y])\right\}+$$

$$+\left\{\delta[A]\left(-\frac{2}{[B]_0}-\frac{1}{[A]_0}\right)+\delta[C]\left(-\frac{2}{[B]_0}-\frac{1}{[C]_0}\right)\right\}\times$$

$$\times\left\{\delta[A](-2k_3[B]_0-k_{-3}[C]_0)+\right.$$

$$\left.+\delta[C](-2k_3[B]_0-k_{-3}[A]_0)\right\} \tag{38}$$

where for emphasis we have subscripted the steady state concentrations. Equation (38) may be simplified to read

$$\frac{1}{2R}\frac{\partial(\delta^2 S)}{\partial t} = (\delta[A])^2\left\{\frac{1}{[A]_0}(\tilde{g}+k_{-1}[Y]+2k_3[B]_0+k_{-3}[C]_0)+\right.$$

$$+\frac{1}{[B]_0}(\tilde{g}+k_{-1}[Y]+k_2[Z]-k_{-2}[C]_0+4k_3[B]_0+$$

$$\left.+2k_{-3}[C]_0)\right\}+(\delta[C])^2\left\{\frac{1}{[B]_0}(k_{-1}[Y]+k_2[Z]+\right.$$

$$+k_{-2}[Y]+4k_3[B]_0+2k_{-3}[A]_0)+\frac{1}{[C]_0}(k_2[Z]+$$

$$\left.+k_{-2}[Y]+2k_3[B]_0+k_{-3}[A]_0)\right\}+$$

$$+(\delta[A]\delta[C])\left\{\frac{1}{[A]_0}(k_{-1}[Y]+2k_3[B]_0+k_{-3}[A]_0)+\right.$$

$$+\frac{1}{[B]_0}(\tilde{g}+2k_{-1}[Y]+2k_2[Z]+k_{-2}[Y]-k_{-2}[C]_0+$$

$$+8k_3[B]_0+2k_{-3}[A]_0+2k_{-3}[C]_0)+$$

$$+ \frac{1}{[C]_0}(k_2[Z] - k_{-2}[C]_0 + 2k_3[B]_0 + k_{-3}[C]_0) \Big\} \quad (39)$$

We now consider the algebraic structure of the result eqn. (39). First of all, the coefficient of the term $(\delta[C])^2$ is strictly positive. In the coefficient of the term $(\delta[A]\delta[C])$ there are two negative terms; it should be noticed, however, that

$$\frac{1}{[B]_0}(k_{-2}[Y] - k_{-2}[C]_0) + \frac{1}{[C]_0}(-k_{-2}[C]_0)$$

$$= \frac{k_{-2}}{[B]_0}([Y] - [C]_0 - [B]_0) > 0$$

so we conclude that the coefficient overall is positive.

Finally, let us consider the coefficient of the term $(\delta[A])^2$. From the steady state condition

$$\frac{d[C]}{dt} = k_2[B]_0[Z] - k_{-2}[C]_0[Y] + k_3[B]_0^2 - k_{-3}[A]_0[C]_0 = 0$$

we may write

$$k_{-2}[C]_0 = \frac{1}{[Y]}(k_2[B]_0[Z] + k_3[B]_0^2 - k_{-3}[A]_0[C]_0)$$

Thus in the coefficient of the term $(\delta[A])^2$, *i.e.* in

$$\frac{1}{[A]_0}(\tilde{g} + k_{-1}[Y] + 2k_3[B]_0 + k_{-3}[C]_0) +$$

$$+ \frac{1}{[B]_0}(\tilde{g} + k_{-1}[Y] + k_2[Z] - k_{-2}[C]_0 + 2k_3[B]_0 + k_{-3}[C]_0)$$

we have

$$k_2[Z] - k_{-2}[C]_0 + 2k_3[B]_0$$

$$= k_2[Z] - \frac{1}{[Y]}(k_2[B]_0[Z] + k_3[B]_0^2 - k_{-3}[A]_0[C]_0) + 2k_3[B]_0$$

$$= k_2[Z]\Big(1 - \frac{[B]_0}{[Y]}\Big) + k_3[B]_0\Big(2 - \frac{[B]_0}{[Y]}\Big) + k_{-3}[A]_0[C]_0$$

$$> 0$$

Moreover, the terms in braces multiplying the variations $(\delta[A])^2$ and $(\delta[C])^2$ taken together compensate the terms in the coefficient of the (possible negative) factor $(\delta[A])(\delta[C])$ for $|\delta[A]| = |\delta[C]| = \epsilon > 0$. Hence, we have demonstrated that, for all the photostationary states considered, the fundamental inequality

$$\frac{\partial(\delta^2 S)}{\partial t} > 0$$

is satisfied and hence, from the thermodynamic stability analysis, we conclude that in every possible mechanistic realization the corresponding photostationary steady state is asymptotically stable. It is important to emphasize that, whereas the linear stability analysis was specific to the mechanisms (and mechanistic "phase boundaries") identified, the thermodynamic stability result pertains to the entire mechanistic "phase plane".

3. Stability analysis of a photogalvanic cell with diffusion

In this section we consider explicitly the role of reactant diffusion in influencing the stability of the photogalvanic system defined by eqns. (9) - (13). A considerable simplification in the analysis is realized if we take advantage of the experimental fact that the concentration of metal ions (Y,Z) is considerably larger than the concentration of the organic dye species (A,B,C). In effect, we may assume that the metal ion concentration is effectively constant; then the system of coupled equations to be considered is

$$\frac{\partial [A]}{\partial t} = D_A \nabla^2 [A] - \tilde{g}[A] + k_{-1}[B][Y] + k_3[B]^2 - k_{-3}[A][C] \quad (40)$$

$$\frac{\partial [B]}{\partial t} = D_B \nabla^2 [B] - \tilde{g}[A] - k_{-1}[B][Y] - k_2[B][Z] + k_{-2}[C][Y] -$$

$$- 2k_3[B]^2 + 2k_{-3}[A][C] \quad (41)$$

$$\frac{\partial [C]}{\partial t} = D_C \nabla^2 [C] + k_2[B][Z] - k_{-2}[C][Y] + k_3[B]^2 - k_{-3}[A][C]$$

$$(42)$$

The corresponding variational equations are

$$\frac{\partial (\delta [A])}{\partial t} = P_A(\delta [A]) + P_B(\delta [B]) + P_C(\delta [C]) \quad (43)$$

$$\frac{\partial (\delta [B])}{\partial t} = Q_A(\delta [A]) + Q_B(\delta [B]) + Q_C(\delta [C]) \quad (44)$$

$$\frac{\partial (\delta [C])}{\partial t} = R_A(\delta [A]) + R_B(\delta [B]) + R_C(\delta [C]) \quad (45)$$

where

$$P_A = -D_A' - \alpha \qquad P_B = \beta \qquad\qquad P_C = -k_{-3}[A]$$

$$Q_A = \alpha + k_{-3}[C] \qquad Q_B = -D_B' - \beta - \gamma \qquad Q_C = \sigma + k_{-3}[A]$$

$$R_A = -k_{-3}[C] \qquad R_B = \gamma \qquad\qquad R_C = -D_C' - \sigma$$

and

$$\alpha = \tilde{g} + k_{-3}[C]$$

$$\beta = k_{-1}[Y] + 2k_3[B]$$

$$\gamma = k_2[Z] + 2k_3[B]$$

$$\sigma = k_{-2}[Y] + k_{-3}[A]$$

If we specify l to be a characteristic length of the photogalvanic cell, then a solution of the set eqns. (43) - (45) consistent with the boundary conditions

$$\delta[A](0,t) = \delta[A](l,t) = \delta[B](0,t) = \delta[B](l,t) = \delta[C](0,t)$$

$$= \delta[C](l,t) \tag{46}$$

is

$$\begin{bmatrix} \delta[A] \\ \delta[B] \\ \delta[C] \end{bmatrix} = \begin{bmatrix} (\delta[A])_0 \\ (\delta[B])_0 \\ (\delta[C])_0 \end{bmatrix} \exp(st) \sin\left(\frac{n\pi\chi}{l}\right) \tag{47}$$

where

$$D' = D\frac{n^2\pi^2}{l^2} \tag{48}$$

and n is an integer. The temporal eigenvalues (here $\{s\} = s_1, s_2, s_3$) of the problem may then be determined by solving

$$\begin{vmatrix} -D_A' - \alpha - s & \beta & -k_{-3}[A] \\ \alpha + k_{-3}[C] & -D_B' - \beta - \gamma - s & \sigma + k_{-3}[A] \\ -k_{-3}[C] & \gamma & -D_C' - \sigma - s \end{vmatrix} = 0 \tag{49}$$

Since it is likely that the diffusion constants D_A, D_B and D_C of the species A, B, and C are very nearly the same, we specify here $D_A = D_B = D_C$; with this choice simple manipulations on the resulting determinant show that

$$s_3 = -D' \tag{50}$$

and the two remaining eigenvalues s_1 and s_2 satisfy the relations

$$s_1 + s_2 = 2D' + \beta + \gamma + \sigma + \alpha > 0 \tag{51a}$$

and

$$s_1 s_2 = (D' + \beta + \alpha + \gamma + k_{-3}[C])(D' + \sigma - k_{-3}[C]) -$$

$$- (\gamma + k_{-3}[C])(\sigma - k_{-3}[C] + k_{-3}[A] - \alpha) \qquad (51b)$$

When expanded the product $s_1 s_2$ has two negative terms, i.e. $k_{-1}[Y] k_{-3}[C]$ and $k_2[Z] k_{-3}[A]$; we have already shown in Section 2.1 that these two terms vanish, so that here again $s_1 s_2 > 0$. Analysis of the discriminant

$$\Delta = (s_1 + s_2)^2 - 4 s_1 s_2 \qquad (52)$$

shows that $\Delta > 0$, from which result we conclude that s_1 and s_2 are real and that s_1 and s_2 are negative. In other words, if it is assumed that the diffusion constants of the species A, B and C are all the same, asymptotic stability of the system, eqns. (40) - (42), is still ensured. Of course, the actual values of the temporal eigenvalues $\{s_1, s_2, s_3\}$ will depend on the values assumed for the diffusion constant D and on the length parameter l which specifies the relevant spatial coordinate of the cell. This point will be explored numerically for the system studied experimentally in ref. 1 in the following section. Before turning to the calculations, however, we remark that, if instead of imposing the constraint $D_A = D_B = D_C$ we consider the general case ($D_A \neq D_B \neq D_C$), an analysis similar to that just reported leads to the conclusion that either (1) all three eigenvalues are negative or (2) there is a single negative (purely real) eigenvalue and two eigenvalues which are complex conjugates. Should the latter possibility be realized in a particular photogalvanic cell, the system would exhibit oscillations which, in principle, could be observed by monitoring the photocurrent. We do not explore this interesting possibility here since the organic dye molecules (A,B,C) of refs. 1 and 2 are so similar; however, it should be possible to design an experimental system where the general case ($D_A \neq D_B \neq D_C$) is realized and then to explore regimes where oscillations may occur. Such an experimental system is under development at the present time in this laboratory.

4. Application to the iron—thionine system

In this section we wish to apply the general considerations of the preceding two sections to the specific photogalvanic cell studied experimentally in ref. 2. In particular, our objective is to determine the stability of the photostationary state(s) of the iron—thionine system, first with respect to variation in the concentration of the metal ion Fe^{3+} (i.e. Y) and then with respect to enhancement in the strength of the irradiance variable $\mathcal{J}$. We consider first the well-stirred case and then analyze subsequently the full reaction—diffusion model.

For the model introduced in ref. 1, it was shown that six possible mechanisms may characterize the reaction of a one-electron redox couple with a two-electron redox couple. However, upon examining the experimental evidence on the iron—thionine system, it was shown in ref. 2 that four of

the six possibilities could be eliminated leaving the two mechanisms A1 B2 C1 and A1 B2 C1. Once again, in the notation of ref. 1, B2 and C1 define the constraints

$$k_3[B] > k_2[Z] \tag{B2}$$

$$k_{-2}[Y] > k_{-3}[A] \tag{C1}$$

while A1 and A2 refer to the inequalities

$$k_{-1}[Y] > k_3[B] \tag{A1}$$

$$k_{-1}[Y] < k_3[B] \tag{A2}$$

For the present, although we shall assume that the conditions B2 and C1 hold, we shall proceed generally in our treatment with respect to the condition A (1 or 2). In the limit when the right-hand side of the conditions B2 and C1 can be neglected (that this simplification is valid for the iron–thionine system will be demonstrated explicitly in later paragraphs), the steady state concentration of C, here denoted $[C]_0$, is given by

$$[C]_0 = \frac{2k_3 a\tilde{g}(k_{-2}[Y] + \tilde{g}) + k_{-2}[Y](\tilde{g} + k_{-1}[Y])^2 - \Delta^{1/2}}{2k_3(k_{-2}[Y] + \tilde{g})^2} \tag{53a}$$

where

$$\Delta = \{4k_3 a\tilde{g}(k_{-2}[Y] + \tilde{g}) + k_{-2}[Y](\tilde{g} + k_{-1}[Y])^2\}k_{-2}[Y](\tilde{g} +$$

$$+ k_{-1}[Y])^2 \tag{53b}$$

From the linear stability analysis presented earlier, we know that the eigenvalues s_1 and s_2 are real and negative. For purposes of computation we take advantage of the constraints B2 and C1 and the (experimental) fact that $[Y] + [B] \approx [Y]$. Hence, the general eqns. (24) effectively collapse to the following simpler relations:

$$s_1 + s_2 = -(\tilde{g} + k_{-1}[Y] + 4k_3[B]_0 + k_{-3}[C]_0 + k_{-2}[Y]) \tag{54a}$$

$$s_1 s_2 = \tilde{g}(2k_3[B]_0 + k_{-2}[Y]) + k_{-1}k_{-2}[Y]^2 + 2k_3 k_{-2}[B]_0[Y] +$$

$$+ k_{-2}k_{-3}[C]_0[Y] + k_{-2}[C]_0(k_{-1}[Y] + 2k_3[B]_0 + k_{-3}[A]_0) -$$

$$- k_{-1}k_{-3}[C]_0[Y] \tag{54b}$$

We remark in passing that our thermodynamic stability analysis has also confirmed the stability of the photostationary state.

It is evident that the actual calculation of the eigenvalues (s_1, s_2) requires knowledge of the steady state concentrations of the interacting species as well as the estimates of the individual rate constants governing the chemical events. We now proceed to identify these factors. We begin by noting that the ratio

$$\frac{k_{-1}{}^2}{k_3}\frac{1}{k_{-2}} \equiv \mathcal{R}$$

can be determined from ref. 2, Table 6. It is found that for an acid solution (0.05 M H_2SO_4)

$$\mathcal{R} \equiv \frac{k_{-1}{}^2}{k_3}\frac{1}{k_{-2}} = 1.052 \times 10^{-2}$$

whereas for a solution in 0.01 M in K_2SO_4 at pH 2.5 it is found that

$$\mathcal{R} \equiv \frac{k_{-1}{}^2}{k_3}\frac{1}{k_{-2}} = 1.1 \times 10^{-2}$$

Since differing values of the individual rate constants appearing in this ratio have been reported in the literature, these ratios will be used to check (for consistency) the values identified later for k_{-1}, k_2 and k_3. For example, Wildes *et al.* [5] have reported the values

$$k_{-1} = 1.2 \times 10^5 \, M^{-1} \, s^{-1}$$

$$k_3 \quad = 2.8 \times 10^8 \, M^{-1} \, s^{-1}$$

$$k_{-3} = 6 \times 10^2 \, M^{-1} \, s^{-1}$$

$$k_{-2} = 6 \times 10^2 \, M^{-1} \, s^{-1}$$

(I)

for kinetics carried out in 50 vol.% aqueous acetonitrile, 0.01 M sulfuric acid and 0.01 M $FeSO_4$; here it is calculated that

$$\mathcal{R}_I = 8.57 \times 10^{-2}$$

A second goup [6] has reported the values

$$k_{-1} = 7.9 \times 10^4 \, M^{-1} \, s^{-1}$$

$$k_3 \quad = 2.4 \times 10^9 \, M^{-1} \, s^{-1}$$

$$k_{-2} = 2.6 \times 10^2 \, M^{-1} \, s^{-1}$$

$$k_{-3} \ll 10^5 \, M^{-1} \, s^{-1}$$

(II)

where these constants were determined for a solution 0.1 N in H_2SO_4; here it is found that

$$\mathcal{R}_{II} = 1.000 \times 10^{-2}$$

Finally, Ferreira and Harriman [7] have reported the following data for a solution at pH 2.5:

$$k_{-2} = (9 \pm 1) \times 10^4 \, M^{-1} \, s^{-1}$$

$$k_{-1} = 7 \times 10^7 \, M^{-1} \, s^{-1}$$

(III)

The rate constant k_3 which governs the dismutation of semithionine (B) is strongly dependent on the polarity of the solution [8]. We shall assume that the value of k_3 for a solution at pH 2.5 is sensibly given by the value $k_3 = 2.4 \times 10^9$ M^{-1} s^{-1}; using this k_3 value and the aforementioned values of k_{-2} and k_{-1}, it is found that

$$\mathcal{R}_{III} = 22.68$$

From these calculations it would appear that the data reported in the paper of Hatchard and Parker [6], case (II), are more nearly consistent with the rate data presented in ref. 2; this conclusion will be useful later in deciding between the rate constants specified in cases (I) and (II). Here, however, we simply complete the specification of experimental parameters by noting (see ref. 2, eqn. (1)) that

$$g = \theta \frac{[A]}{[A]_D} \phi_B g_0$$

so that in our notation

$$\tilde{g} = \theta \frac{1}{[A]_D} \phi_B g_0$$

From ref. 2, for the experiment performed in 0.05 M H_2SO_4, $\phi_B = 1$, $[A]_D = 7.8$ μm, $g_0 = 0.41 \times 10^{-3}$ M s^{-1} and $\theta = 0.2$ so that $\tilde{g} = 10.5$ s^{-1}. Finally we have

$$a = [A]_D = 7.8 \ \mu m$$

and

$$[Z] = 5 \times 10^{-4} \ M$$

Using the rate constants listed in case (I) and the experimental parameters noted in the preceding paragraph, it is found that, for $[Y] = 10^{-3}$ M, $k_{-2}[Y] = 0.6$ s^{-1} and $k_{-3}a = 4.68 \times 10^{-3}$ s^{-1}. Thus

$$k_{-2}[Y] \gg k_{-3}a > k_{-3}[A]_0$$

and the condition C1 is satisfied. From the work of Hardwick [9] it is known that the ratio of k_{-2} to k_2 is bracketed between the values

$$450 < \frac{k_{-2}}{k_2} < 10^4$$

so that, using the value of k_{-2} in case (I), we may conclude that

$$1.33 \ M^{-1} \ s^{-1} < k_2 < 6 \times 10^{-2} \ M^{-1} \ s^{-1}$$

and hence that

$$6.65 \times 10^{-4} \ s^{-1} < k_2[Z] < 3 \times 10^{-5} \ s^{-1}$$

Even if $[B]_0$ is somewhat less than about 10^{-9} M, we find that $k_3[B]_0 = 2.8 \times 10^{-1}$ s^{-1}. Thus

$$k_3[B]_0 \gg k_2[Z]$$

and the condition B2 is easily satisfied. Using eqns. (53) and the relationship between $[C]_0$, $[A]_0$ and $[B]_0$ it is found that

$$[C]_0 = 6.04 \times 10^{-6} \text{ M}$$

$$[A]_0 = 1.64 \times 10^{-6} \text{ M}$$

$$[B]_0 = 1.14 \times 10^{-7} \text{ M}$$

From these values, we determine that $k_{-1}[Y] = 120$ s^{-1} and $k_3[B]_0 = 3.19$ s^{-1} from which it follows that

$$k_{-1}[Y] > k_3[B]_0$$

and hence the overall mechanism here will be A1 B2 C1. Incidentally, these estimates of the steady state concentrations may be compared with those calculated from expressions given in refs. 1 and 2. It is assumed in ref. 2 that the concentration $[B]_0$ is so small it may be neglected. Then

$$[C]_0 + [A]_0 \approx a$$

and, for the mechanism A1 B2 C1 where it is assumed further [2] that $k_{-1}[Y] \gg k_3[B]$, it is found that $[A]_0$ satisfies the quadratic equation

$$\frac{k_3 \tilde{g}^2 [A]_0^2}{k_{-1}^2 k_{-2}[Y]^3} + [A]_0 = a$$

Solution of this quadratic shows that $[A]_0 = 1.34 \times 10^{-6}$ M and hence that $[C]_0 = 6.46 \times 10^{-6}$ M. We shall comment on these estimates in relation to those computed earlier in a later paragraph.

We now use the rate constant data summarized in case (II) and repeat the calculations presented in the preceding paragraph. Starting from eqns. (53), we calculate

$$[C]_0 = 7.38 \times 10^{-6} \text{ M}$$

$$[B]_0 = 2.83 \times 10^{-8} \text{ M}$$

$$[A]_0 = 3.95 \times 10^{-7} \text{ M}$$

Then we find that $k_{-1}[Y] = 79$ s^{-1} and $k_3[B]_0 = 67.9$ s^{-1} so that

$$k_{-1}[Y] > k_3[B]_0$$

and hence condition A1 is satisfied. Next, using Hardwick's data the estimate for the rate constant k_2 can be bracketed between the values

$$2.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} < k_2 < 0.577 \text{ M}^{-1} \text{ s}^{-1}$$

so that

$$k_2[Z] < 2.89 \times 10^{-4} \text{ s}^{-1}$$

Now, $k_3[B]_0 = 67.9 \text{ s}^{-1}$ so that

$$k_3[B]_0 \gg k_2[Z]$$

and condition B2 is satisfied. Finally, we determine that $k_{-2}[Y] = 0.26 \text{ s}^{-1}$ and $k_{-3}[A]_0 < 0.040 \text{ s}^{-1}$ (since $k_{-3} \ll 10^5 \text{ M}^{-1} \text{ s}^{-1}$) and so

$$k_{-2}[Y] \gg k_{-3}[A]_0$$

Again we find that condition C1 is satisfied. Hence, using the rate constants summarized in case (II) we again determine the mechanism to be A1 B2 C1. A calculation of the steady state concentrations $[C]_0$ and $[A]_0$ using expressions given in refs. 1 and 2 yields the following results:

$$[C]_0 = 7.58 \times 10^{-6} \text{ M}$$

$$[A]_0 = 2.16 \times 10^{-7} \text{ M}$$

As a final calculation to determine which set of rate constraints is most consistent with the experimental findings of ref. 2, we consider the rate constant data summarized in case (III). We estimate that

$$[C]_0 \approx 10^{-11} \text{ M}$$

$$[B]_0 \approx 10^{-9} \text{ M}$$

$$[A]_0 \approx 7.8 \times 10^{-6} \text{ M}$$

Here, the rate constant k_2 may be bracketed between the values

$$9 \text{ M}^{-1} \text{ s}^{-1} < k_2 < 2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$$

Even with these rather more diverse estimates of steady state concentrations and rate constants, we again conclude that the mechanism operative in this range of metal ion concentration and irradiance is A1 B2 C1. From the expressions in refs. 1 and 2 we may also estimate

$$[A]_0 = 7.8 \times 10^{-6} \text{ M}$$

a number which happens to coincide with our earlier estimate because $[C]_0 \approx 0$ and the effective steady state concentration $[B]_0$ is neglected at the very outset in the approach taken in ref. 2.

We are now in a position to decide which set of rate constants leads to results in closest correspondence with the experimental findings of ref. 2. From ref. 2, Fig. 1, where we have $\theta = 0.20$, $[Y] = 10^{-3}$ M and $\log \{f/(1-f)\} = -0.5$, then given that $[A]_D = 7.8 \times 10^{-6}$ M we calculate $[C]_0 = 1.87 \times 10^{-6}$ M. This calculation allows us to eliminate from further consideration the rate data of case (III). The $[C]_0$ value estimated from the rate data of cases (I) and (II) (using eqns. (53) and, as well, expressions from

refs. 1 and 2) is certainly of the same order of magnitude as the value taken from the experimental data of ref. 2, although the magnitude of the $[C]_0$ value calculated in both cases is off by a factor of about 3 from the experimental estimate. This is probably to be expected since we neglected in our treatment in this work any consideration of diffusion and surface aspects of the electrode kinetics. Of the two cases (I) and (II) we settle on the rate constant data summarized in case (II) since the value of the ratio $\mathcal{R}$ is more nearly consistent with that computed directly from the evidence in ref. 2. Having now values of the rate constants at our disposal we can calculate the eigenvalues s_1 and s_2 for various concentrations of the metal ion Y, and for different values of the irradiance variable $\tilde{g}$. This, in turn, will allow us to reach definite conclusions regarding the stability of the mechanisms A1 B2 C1 and A2 B2 C1 as a function of metal ion concentration and system illumination.

We present in Table 1 a summary of our linear stability analysis for the iron–thionine system for the well-stirred case. The calculations were performed using the rate constant data displayed as case (II) (with the value of k_3 specified in case (I)) for five different values of the concentration of the metal ion Fe^{3+} (denoted Y), and three different values of the irradiance variable θ (or $\tilde{g}$). For each of the calculations the conditions A1(A2), B1(B2) and C1(C2) were checked in order to determine the mechanism operative in that regime of $\{[Y], \tilde{g}\}$; the mechanism so determined is listed in the table. Before proceeding to an interpretation of the stability analysis it should be noted that the mechanism can change from A2 B2 C1 to A1 B2 C1 either with increase in the concentration variable [Y] or with decrease in the irradiance variable $\tilde{g}$. That this changeover in mechanism may occur has been noted already in refs. 1 and 2.

We consider now the eigenvalues listed in Table 1. Although the formal analysis presented in Sections 2 and 3 ensures that for every possible mechanism the two temporal eigenvalues should be negative, the numerical results reported in Table 1 for an actual experimental system (the iron–thionine system) are in themselves quite interesting. For a particular choice $\{[Y], \tilde{g}\}$, each pair of eigenvalues is characterized by the fact that for all cases one temporal eigenvalue is larger in magnitude than the other eigenvalue (sometimes by as much as three orders of magnitude). Now, in considering the asymptotic stability of a non-linear system, it is always the eigenvalue closest to zero that governs the stability of the system. Given the closeness to zero of one temporal eigenvalue in each case, it is interesting to speculate whether the explicit consideration of diffusion and/or concentration effects associated with electrode kinetics may result in the cross-over of this eigenvalue from a negative to a positive value. Should this occur for certain mechanisms, the photogalvanic cell when operated in that regime of experimental constraints would be marginally stable and the overall efficiency of the cell would be impaired. This more complex problem will now be considered.

In their study of the optimum efficiency of photogalvanic cells for solar energy conversion, Albery and Archer [10] give $l = 0.1$ mm as the cell

TABLE 1

Stability eigenvalues of the iron–thionine photogalvanic cell for various values of metal ion concentration ($Fe^{3+} \equiv Y$) and system illumination for the well-stirred initial condition

	$[Y] = 10^{-4} M$	$[Y] = 7.2 \times 10^{-4} M$	$[Y] = 7.5 \times 10^{-4} M$	$[Y] = 10^{-3} M$	$[Y] = 10^{-2} M$
$\tilde{g} = 52.5 \text{ s}^{-1}$ ($\theta = 1.0$)	A2 B2 C1 −131 −17.1	A2 B2 C1 −326 −19.1	A2 B2 C1 −333 −19.1	A2 B2 C1 −390 −18.8	A1 B2 C1 −1616 −14.8
$\tilde{g} = 10.5 \text{ s}^{-1}$ ($\theta = 0.20$)	A2 B2 C1 −102 −4.55	A2 B2 C1 −296 −4.24	A1 B2 C1 A1≈A2 B2 C1 −303 −4.23	A1 B2 C1 −357 −4.16	A1 B2 C1 −1333 −4.19
$\tilde{g} = 3.68 \text{ s}^{-1}$ ($\theta = 0.07$)	A2 B2 C1 −97.7 −1.67	A1 B2 C1 −284 −1.57	A1 B2 C1 −291 −1.57	A1 B2 C1 −340 −1.56	A1 B2 C1 −1079 −2.74

length (or distance between electrodes) in a typical photogalvanic cell. Using this value together with $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ as a "typical" diffusion constant, we may calculate the temporal eigenvalues $\{s\}$ corresponding to the system, eqns. (40) - (42). In fact, since it is found [10] that the efficiency of a photogalvanic cell is dependent on a sensitive interplay between the length l, the absorbance length, the generating length and the reaction length, it is of interest to compute the eigenvalues $\{s\}$ for different values of the cell length l. Different choices of l change the (reduced) diffusion coefficient D'_i (see eqn. (48)), and in Table 2 we report values of $\{s\}$ for three different choices of D'; these calculations were performed assuming the particular mechanism A1 B2 C1 and for the rate data summarized as case (II) in the preceding discussion. We also specify the (intermediate) metal ion concentrations, $[Y] = 10^{-3} M$ ($[Fe^{3+}]$) and $[Z] = 5 \times 10^{-4} M$ ($[Fe^{2+}]$), and the system illumination, $\tilde{g} = 10.5 \text{ s}^{-1}$. The values of $\{s_1, s_2, s_3\}$ so calculated may then be compared with the values of $\{s_1, s_2\}$ determined for the well-stirred system where the latter are included in Table 2 for the mechanism A1 B2 C1 as well. We comment on these results in the following section.

5. Conclusions

In the design of photogalvanic cells for solar energy conversion, a number of factors are thought to play an important role in influencing the efficiency of such devices. The first clear analysis of this problem was presented in 1977 by Albery and Archer [10]. In their study these authors pointed out that the performance of a photogalvanic device depends on the cell photochemistry, the homogeneous kinetics, the mass transport of reactants and the electrode kinetics. Specifically, they analyzed the variation of

TABLE 2

Stability eigenvalues of the iron–thionine photogalvanic cell taking reactant diffusion into account

$D' = \pi^2 D/l^2$ (s^{-1})	s_1 (s^{-1})	s_2 (s^{-1})	s_3 (s^{-1})
0.0987 ($l = 0.1 \times \sqrt{10}$ mm)	−4.25	−357.0	−0.0987
0.987 ($l = 0.1$ mm)	−5.14	−358.0	−0.987
9.87 ($l = 0.1/\sqrt{10}$ mm)	−14.0	−367.0	−9.87
Well-stirred case	−4.16	−357.0	

$[Fe^{3+}] = [Y] = 10^{-3}$ M, $[Fe^{2+}] = [Z] = 5 \times 10^{-4}$ M and $\tilde{g} = 10.5$ s^{-1}.

the power output with the concentrations of the redox couple, with their transport and kinetic parameters and with the dimensions of the cell, and concluded that although the power conversion efficiency could be as high as 18% a more realistic estimate would be in the range 5 - 9%. However, many authors (see refs. 3 and 4 and references cited therein) have drawn attention to the importance of analyzing the stability of coupled non-linear reaction–diffusion systems. In studying such non-linear systems, phenomena such as "overshoots", oscillations and even chemical "chaos" are found to occur, often in systems which appear to be quite harmless mathematically. Were they to occur in a photogalvanic device, such phenomena would certainly influence the efficiency of the cell in a significant way. Accordingly, in this work we have addressed the problem of stability of photochemical mechanisms for photogalvanic cells, first for the case where the system is assumed to be well stirred and then for the case where reactant diffusion is taken into account explicitly. For definiteness we have focused on a chemical model introduced recently by Albery et al. [1] which incorporates the main features of a common type of photogalvanic cell. These authors considered a photoredox system in which a one-electron redox pair (e.g. an inorganic couple) reacts with a two-electron redox couple (an organic dye), and demonstrated that there are six possible mechanisms by which the system can react. For a given set of rate constants, which mechanism is found depends on the concentrations of the reacting species and on the system illumination. The principal concern of this work was to assess the stability of the photostationary state(s) accessible to the system in each concentration–irradiance regime.

Considering first the well-stirred case, the analysis of the six possible mechanisms identified in ref. 1 was carried out using a linear stability analysis as well as the thermodynamic stability analysis. Particular attention was paid to those regions of the overall kinetic "phase diagram" where two (or more) mechanisms may pertain. In order to facilitate the application of our results to specific experimental situations, we have presented explicit expressions characterizing the stability for all photochemical schemes described by eqns. (1) - (3) consistent with the (experimental) requirement that the

concentration of metal ion exceeds the concentration of organic dye. Our concern in the preceding section was to demonstrate how such an application could be carried out in a specific case and to indicate the insights that follow from the stability analysis. There we considered the iron–thionine system, since already in ref. 2 a characterization had been made of the probable photochemical mechanism in certain regimes of concentration and system illumination. We suggest that the analysis presented in refs. 1 and 2 for the iron–thionine system may be complemented by the data summarized in Table 1. It should be recalled that the eigenvalues listed in Table 1 for each case are both negative (as was forecast by the analyses in Section 2). However, by utilizing actual experimental data on the iron–thionine system, it was found that one eigenvalue of each pair is close to zero. This raises the possibility that a more general analysis, one which would incorporate diffusion and/or concentration effects associated with electrode kinetics, may reveal the cross-over of this eigenvalue to a negative value, thereby suggesting that operation of the photogalvanic device in that regime of parameter space may result in a photostationary state characterized by marginal stability. This possibility was considered in Section 3, and there it was found that, provided the diffusion coefficients of A, B and C were the same, (asymptotic) stability of the photostationary state was still guaranteed. Only if the diffusion coefficients (of A, B and C) were assumed to be different is this stability compromised, inasmuch as the onset of oscillations becomes possible. We did not explore this possibility in greater detail here since, in the experimental system studied in ref. 1, it is most probable that the diffusion coefficients of thionine (A), the semithionine radical (B) and leucothionine (C) are essentially the same. As noted in Section 3 we are presently investigating an experimental situation where $D_{A'} \neq D_{B'} \neq D_{C'}$ may be realized; the onset of oscillations in this system will be observed by monitoring the photocurrent generated by the photogalvanic cell. For the iron–thionine system, however, even though stability is still ensured when diffusion is incorporated, the calculations reported in Section 4 reveal an interesting dependence on the cell length parameter l. For a given mechanism and for a specific choice of diffusion constant, concentration of metal ion and system illumination, the results in Table 2 show that, as regards stability properties, the photogalvanic cell behaves essentially like a well-stirred system for the cell length $l = 0.1$ mm, the value of l relevant to the experimental studies of refs. 1, 2 and 10. Only when l becomes less than 0.1 mm is a significant shift in the eigenvalues $\{s_1, s_2\}$ to more negative values found. Even if this shift in $\{s_1, s_2\}$ were to reflect enhanced stability of the overall reaction–diffusion system, it may be questioned whether such an enhancement is desirable. Albery and Archer [10] point out that if the cell length becomes too small the dark electrode will interfere with the reaction of the semithionine intermediate B on the illuminated electrode; specifically, some B will be lost by reaction with metal ion Fe^{3+} and, in effect, the cell becomes too efficient with respect to removal of B, a most undesirable feature. Thus, in the design of photogalvanic devices there seems to be a trade off between

optimizing the overall efficiency of the cell and choosing conditions to ensure the stability of the photostationary state.

Even within the context of the present analysis it is important to stress that instabilities may arise because of system illumination effects alone. We remind the reader that, although the quantum efficiency for production of leucothionine will have its maximum value of unity at low irradiance values [1], Albery *et al.* point out that low irradiance devices have such low efficiencies that such photogalvanic devices cannot be successful; they conclude that it is essential to drive the system sufficiently hard so that the A2 B2 C1 mechanism is operative. However, increased system illumination has certain limitations, both operational (*i.e.* experimental) and theoretical. With respect to the latter qualification, it has been noted by Nitzan *et al.* [11] that, if the rate constants characterizing the chemical events taking place in the system are characterized by a non-negligible temperature dependence (*e.g.* are of Arrhenius form with $E_a \approx RT$), then systems subject to high light flux conditions may be driven into unstable thermochemical regimes. The idea here is that, since the radiant energy incident on the system will at least in part be degraded to thermal energy, the accompanying rise in temperature of the system will affect the chemistry (through the temperature-dependent rate constants) and in certain cases the consequent change in the kinetics may affect the ambient temperature. Thus a dynamic situation can be realized wherein a non-linear feedback mechanism comes into play between the photochemical and physical processes in the system. Nitzan *et al.* [11] have demonstrated that the absorption of light by some, but not all, species of a chemical reaction (even a simple isomerization), followed by a radiationless transition and ultimate conversion of light into heat on a time scale short compared with the chemical reaction time scale, gives rise to the possibilities of multiple steady states, damped oscillations in state variables, hysteresis and instabilities. And, in investigating non-equilibrium phenomena in the kinetics of photochemical ozone production, Kozak *et al.* [12] have shown that under certain conditions the approach to the steady state may be characterized by considerable overshoots in the composition variables and the temperature. These studies suggest that, if a photogalvanic cell is driven very hard, non-linear effects may modulate considerably the evolution to and maintenance of a photostationary state. We intend to explore this thermal feedback mechanism in a subsequent contribution, as well as the important role played by differential electrode kinetics *per se* in influencing the dynamic stability of photogalvanic devices.

Acknowledgments

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