Semiconductors' Photoelectrochemistry: A Kinetic and Thermodynamic Analysis in the Light of Equilibrium and Nonequilibrium Models

P. Salvador*

Department Matemáticas e Informática, Universidad de las Islas Baleares, 07071 Palma, Spain

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Kinetic and energetic aspects of the photoinduced transfer of charge at the semiconductor−electrolyte interface are analyzed in the light of the equilibrium, conventional photoelectrochemical model (A) attributable to Gerischer, the irreversible, stochastic model (B) proposed by Williams and Nozik, and the nonequilibrium, irreversible model presented here. On the basis of detailed balance and local microscopic reversibility principles, Gerischer's model presents a complete theoretical framework able to describe the kinetic behavior of a photoelectrochemical cell and adopt the quasi-Fermi level formalism as an approach to nonequilibrium, illumination conditions Although model A considers entropy loss as unavoidable (the entropy increases to a maximum near equilibrium), it is not able to predict the time dependent entropy term which characterizes any irreversible process (nonequilibrium conditions). By contrast, model B considers detailed balance and microscopic reversibility principles to be incompatible with the existence of irreversibility, which constitutes a handicap for describing interfacial charge-transfer rate constants under illumination. Moreover, the stochastic model does not take into account the entropy that must be lost in any photoelectrochemical reaction. To overcome the limitations of models A and B, a new irreversible approach, model C, built up on the basis of nonequilibrium thermodynamics and able to reconcile the irreversible character of photoelectrochemical reactions with the production of entropy, is presented here. Identical kinetic behavior is predicted by equilibrium model A and nonequilibrium model C, since both models compute interfacial charge-transfer rate constant ratios in accord with detailed balance and microscopic reversibility principles. The physical meaning of the nonequilibrium quasi-Fermi energy as well as its thermodynamic implications in concepts like photogenerated free energy and entropy loss in a photoelectrochemical reaction are reexamined in the light of the Gibbs expression. A new energy balance formalism based upon the concepts of photoelectrochemical affinity and entropy production is introduced.

I. Introduction

A significant controversy exists in the literature between two different models for photoinduced reactivity at the semiconductor (sc)−electrolyte interface.[1−10] One is the statistical, conventional photoelectrochemical model invoked by Gerischer (model A). In this model, the kinetics and energetics of charge carriers is approximated by an analytical treatment based on equilibrium, statistical mechanics principles, and implemented with the nonequilibrium quasi-Fermi level formalism, a useful approach for describing the nonequilibrium conditions produced by illumination at the sc−electrolyte junction.[1−3] The other is the so-called stochastic model proposed by Williams and Nozik (model B), where the charge-transfer process is considered to take place as individual events (irreversible photoinjection), each thermalized carrier in the sc having the potential of its respective band edges.[4−5] The controversy is centered on two main points: (1) the existence of a light intensity threshold for photoconversion processes and (2) the usefulness of nonequilibrium quasi-Fermi level formalism for describing photoelectrochemical reactions, both from a kinetic and a thermodynamic point of view.

With respect to the first point, in agreement with classical theories of photoinduced molecular electron-transfer reactions, the stochastic model rejects the existence of a light threshold

for spontaneous interfacial transfer of photogenerated charge carriers (incipient product formation).[9] The conflict apparently arises because of a questionable interpretation of the following Gerischer's statement: "...a threshold in illumination intensity must be surpassed to reach the *driving force* for photoelectrolysis of water".[2] In fact, this claim has been interpreted as a prediction of the existence of a light intensity threshold before the photoinduced electron-transfer reaction can be spontaneou.[5,9] However, a correct interpretation of Gerischer's statement must take into account the actual meaning of the term *driving force* used by Gerischer. The key is probably in another statement of Gerischer, "...the *driving force* for water decomposition has to overcome the cell voltage 1.23 eV, to drive the process in the right direction".[1] Since $E^o(H^+/H_2) - E^o(O_2/H_2O) = 1.23$ eV is the minimum energy needed for O_2 and H_2 to be evolved from water under standard conditions, it seems evident that Gerischer did never refer to a light threshold for the appearance of photocurrent (i.e., incipient O_2 and H_2 generation) but to a threshold for net water photoelectrolysis (i.e., formation and separation of O_2 and H_2 at 1 atm), which is only possible when the photocurrent reaches a critical value. This second kind of threshold has been observed experimentally with $SrTiO_3$ electrodes,[7] whereas the light intensity threshold for photocurrent appearance (incipient product formation) has never been reported. A theoretical demonstration that the conventional photoelectrochemical model predicts no threshold in photocur-

* Corresponding author. Fax: 34-971-173003. E-mail: dmipss9@ps.uib.es. On leave from the Instituto de Catálisis y Petroleoquímica, CSIC, Spain.

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rent as a function of light intensity has been given recently.[7,8] Further emphasis on this point will be given along this paper.

As for the second point, the stochastic model rejects the applicability of the nonequilibrium quasi-Fermi level formalism to photoelectrochemical reactions, arguing that it is based upon local, statistical detailed balance and, therefore, cannot be a good approximation for describing photoreactions showing high quantum efficiencies, as it is the case for water photoelectrolysis at oxide sc electrodes (eg., TiO_2 and $SrTiO_3$), where interfacial electron transfer is a highly irreversible process analogous in some respects to photoemision into vacuum.[4] Therefore, Williams and Nozik proposed a different approach able to describe charge transfer processes as individual events rather than statistically. However, this assumption generates serious drawbacks. On one hand, it implicitly invalidates the application of a conventional kinetic analysis, like that used by Gerischer, on the basis of rate expressions described by deterministic differential equations involving continuous concentration variables.[11−12] On the other hand, it must be remarked that any photoelectrochemical model non based on principles of detailed balance and microscopic reversibility, as is the case for the stochastic model, not only rejects the axiom that equilibrium in the dark must allways be achieved but has to postulate a new analytical treatment able to describe the rate constant ratios involved in interfacial, photoinduced charge-transfer kinetics.[8] Since no attempt has been made up to date in this sense, an evaluation of the kinetic and thermodinamic implications of the irreversible model proposed by Williams and Nozik is not possible.

A new approach to the idea of irreversibility, different from that given by the stochastic model, and compatible with the quasi-Fermi level formalismin, can be obtained with the help of nonequilibrium thermodynamics, the branch of thermodynamics dealing with irreversible processes. Also accepting detailed balance and microscopic reversibility principles, nonequilibrium thermodynamics, which are built up upon the basis of phenomenological relationships between thermodynamic forces and fluxes, introduces the entropy production as a new concept for defining the entropy balance equation not present in Gerischer's model. While equilibrium thermodynamics is able to predict that in an isolated system the entropy increases to a maximum defined by the equilibrium conditions (the highest degree of disorder is generated), nonequilibrium thermodynamics predicts that under stationary conditions the entropy generated approaches a minimum. Both thermodynamic approaches, the equilibrium and the nonequilibrium picture, consider entropy loss as unavoidable as long as photocurrent is flowing. This contrast with the stochastic approach which, although considering irreversibility, is not able to take into account the unavoidable entropy term that must be present in any thermodynamic framework.

This work addresses the concepts of nonequilibrium and irreversibility in photoelectrochemistry. With this aim, we start in section II with a systematic analysis of Gerischer's model both from a kinetic and a thermodynamic point of view. The physical meaning of the controversial quasi-Fermi level formalism, as well as its kinetic and thermodynamic implications in concepts like photogenerated free energy and entropy loss, are reexamined and clarified in section II. In an attempt to further the understanding of the concept of irreversibility, a new irreversible, photoelectrochemical approach based on nonequilibrium thermodynamics principles is made in section III. A new energy balance formulation not contemplated by Gerischer, which is built on the basis of nonequilibrium concepts such as

photoelectrochemical activity and entropy production, is presented there. Thermodynamic predictions of this new approach, such as those concerning the relationships between the driving force of a photoelectrochemical reaction (photoelectrochemical activity), the photocurrent intensity and photogenerated free energy stored, as well as the way in which they are influenced by kinetic, interfacial charge transfer parameters (nature of the interaction between the sc surface and the electrolyte), are also presented in section III. Finally, a comparative analysis of the three photoelectrochemical approaches, namely, the conventional (A), the stochastic (B), and the new nonequilibrium model (C) presented here, is exposed in section IV.

II. The Conventional Photoelectrochemical Model

Essentially, the conventional photoelectrochemical model is a kinetic model based on statistical thermodynamic principles of detailed balance and microscopic reversibility. The Boltzman statistical distribution of electrons and holes among the available energy levels of a nondegenerated sc under thermal equilibrium is expressed with the help of the concept of Fermi energy, E_F:

$$n_o(x) = N_C \exp-\left(\frac{E_C - E_F}{kT}\right) \tag{1}$$

$$p_o(x) = N_V \exp-\left(\frac{E_F - E_V}{kT}\right) \tag{2}$$

where $n_o(x)$ and $p_o(x)$ are the local equilibrium concentrations of electrons and holes at position x (see Figure 1A), E_C and E_V are the local position of the conduction and valence band edges and N_C and N_V are the effective local density of states at the bottom of the conduction band (CB) and at the top of the valence band (VB), respectively. The Fermi energy represents the electrochemical potential of electrons and holes. Since the definition of E_F takes into account the existence of internal thermal equilibrium in the sc, according to the mass action law the product of electrons and holes concentration must be constant:

$$n_o(x)p_o(x) = n_i^2 = N_C N_V \exp-\left(\frac{E_g}{kT}\right) \tag{3}$$

n_i being the concentration of charge carriers in the intrinsic material where $n_o = p_o = n_i$ and E_g the band gap energy. Since the electrochemical potential of the electrolyte is defined by the redox potential $E_{redox}(A^-/A)$ (see Figure 1A), according to the Fermi−Dirac statistics, the existence of thermodynamic equilibrium between the sc and the electrolyte requires that

$$E_F = E_{redox}(A^-/A) \tag{4}$$

The application of the principle of detailed balance under equilibrium conditions in the dark allows to determine the rate constant ratios for interfacial transfer of CB electrons and VB holes. In fact, the absence of net electron flux crossing the interface at equilibrium (identical anodic and cathodic flux) allows us to write for the CB charge-transfer process that

$$n_{so}k_n[A] = k_n^{-1}[A^-] \tag{5}$$

where n_{so} is the surface equilibrium concentration of CB electrons (i.e., at $x = 0$), k_n and k_n^{-1} are the forward and backward rate constants for electron transfer from the CB edge to A acceptor species and from A^- donors to CB energy levels,
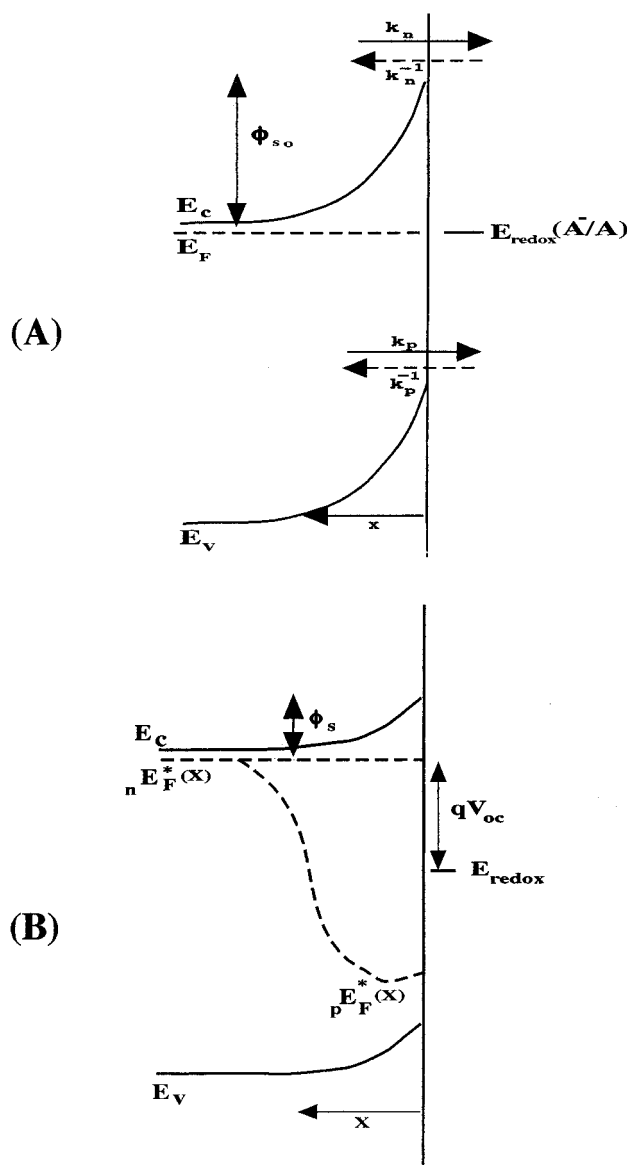
Figure 1. Energy diagram of the sc–electrolyte interface under (A) Equilibrium in the dark, where $E_F = E_{redox}(A^-/A)$; k_n and k_p represent the forward rate constants for injection of CB electrons into A acceptor species and for injection of VB holes into A^- donor species, respectively, while k_n^{-1} and k_p^{-1} are the backward rate constants for injection of electrons from A^- donor species into CB energy levels and for injection of holes from A acceptor species into VB energy levels, respectively. (B) Illumination flux Φ_o and open-circuit conditions, where the photogenerated free energy is represented by the open-circuit voltage $qV_{oc} = E_{nF}^* - E_{redox}$, $(E_{nF}^*)_s$ representing the quasi-Fermi energy for electrons at $x = 0$, given by (8) (V_{oc} depends exponentially on Φ_o through (12)); E_{pF}^* represents the quasi-Fermi energy for holes, given by (9).

respectively, and [A] and $[A^-]$ are the respective concentrations of electrolyte acceptors and donors. An analogous expression can be written for the VB charge-transfer process:

$$p_{so}k_p[A^-] = k_p^{-1}[A] \qquad (6)$$

where p_{so} is the surface equilibrium concentration of VB holes (i.e., at $x = 0$) and k_p and k_p^{-1} are the forward and backward rate constants for hole transfer from the VB edge to A^- donor species and from A acceptors to VB energy levels, respectively. From (5) and (6) the following equilibrium constants are obtained:

$$K_n = \frac{k_n}{k_n^{-1}} = \frac{1}{n_{so}}\frac{[A^-]}{[A]} \quad K_p = \frac{k_p}{k_p^{-1}} = \frac{1}{p_{so}}\frac{[A]}{[A^-]}$$

Moreover, on the basis of the microscopic reversibility principle, Gerischers' model assumes that equilibrium constants K_n and K_p maintain their values away from equilibrium, which allows to obtain a kinetic description of photoinduced, interfacial transfer of charge. So, for a n-type sc under short circuit conditions, the continuity principle establishes that, in the absence of surface recombination, the photogenerated hole flux arriving to the interface, $\eta\phi_o$ (η being the quantum efficiency for electron–hole separation and ϕ_o the absorbed photon flux) must equal the net hole flux crossing the interface, which leads to the following expression for the stationary photocurrent intensity (A cm^{-2})

$$J_{ph,st} = q\eta\phi_o = q[p_s^* k_p[A^-] - k_p^{-1}[A]] =$$
$$q[p_s^* k_p[A^-] - p_{so}k_p[A^-]] = qk_p[A^-](p_s^* - p_{so}) \quad (7)$$

According to (7), for $\eta\phi_o > 0$ it must be $J_{ph,st} > 0$, which means absence of light intensity threshold for photoinduced transfer of charge at the illuminated sc–electrolyte interface.

II.1. Nonequilibrium Illumination Conditions: The Quasi-Fermi-Level Formalism. A concept widely used to describe nonequilibrium sc conditions is the nonequilibrium quasi-Fermi energy for electrons, E_{nF}^*, and holes, E_{pF}^*, which was introduced by Shockley for describing p–n junctions[13] and used by the first time in photoelectrochemistry by Gerischer.[14] Operationally the quasi-Fermi energy for electrons and holes is defined as[13]

$$E_{nF}^*(x) = E_C + kT\ln\left(\frac{n^*(x)}{N_C}\right) \qquad (8)$$

$$E_{pF}^*(x) = E_V - kT\ln\left(\frac{p^*(x)}{N_V}\right) \qquad (9)$$

Some disagreement exists about the physical meaning of E_{nF}^* and E_{pF}^*. For some authors they exclusively describe the excess population of photogenerated carriers $n^*(x)$ and $p^*(x)$ in their respective bands, but not the nonequilibrium population of carriers at any other bulk or surface energy level in the forbidden sc gap.[15] For other authors, by similarity with the concept of Fermi energy, the quasi-Fermi formalism describes the occupational probability of photogenerated electrons and holes among their respective bands and defect states under nonequilibrium conditions.[4] Nevertheless, both interpretations agree that $n^*(x)p^*(x) > n_i^2$, so that the mass action law is no longer satisfied away from equilibrium. From a kinetic point of view both interpretations are equally valid when dealing with interfacial transfer of thermalized, photogenerated carriers between sc bands and electrolyte energy levels.

II.2. The Photogenerated Free Energy in the Light of the Quasi-Fermi Level Formalism. Some confusion exists in semiconductor photoelectrochemistry literature about the meaning of photogenerated free energy in relation with the quasi-Fermi level formalism. It is well-established according to Boltzman approximation the open-circuit voltage, V_{oc} (i.e., the photovoltage measured under open-circuit conditions), which represents the maximum effective energy output of a solar cell at a given illumination intensity, cannot exceed the difference in the quasi-Fermi level of electron and holes at the sc surface[16] (see Figure 1B).

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$$qV_{oc} \leq (E_{nF}^*)_s - (E_{pF}^*)_s = E_g + kT \ln \frac{n_s^* p_s^*}{N_C N_V} \qquad (10)$$

with the subindex s representing local values at the sc surface (i.e., at $x = 0$). While in a p–n solid junction $qV_{oc} = (E_{nF}^*)_s - (E_{pF}^*)_s$,[16] in a liquid junction $qV_{oc} = (E_{nF}^*)_s - E_{redox} < (E_{nF}^*)_s - (E)_{pFS}^*$,[15] the equality in the last case only being possible when $(E_{pF}^*)_s = E_{redox}$, i.e., for $p_s^* = p_{so}$, a situation which, according to (7), is only possible under equilibrium conditions in the dark (i.e., for $\phi_o = 0$). Equivalent to qV_{oc} is the thermodynamic concept of Gibbs energy of photogenerated electron–hole pairs, ΔG, which under conditions of constant temperature and pressure represents the energy available for redox reactions.[1,9] If we identify qV_{oc} with ΔG, we have necessarily to admit that under nonequilibrium illumination conditions

$$\Delta G = (E_{nF}^*)_s - E_{redox} < (E_{nF}^*)_s - (E_{pF}^*)_s \qquad (11)$$

Equation 11 contradicts the generally accepted idea that $(E_{nF}^*)_s - (E_{pF}^*)_s$ represents the free energy of photogenerated electron–hole pairs in a photoelectrochemical cell.[1,9]

On the other hand, the conventional expression for V_{oc} in a regenerative photoelectrochemical cell[7]

$$V_{oc} = \frac{kT}{q} \ln \frac{n_S^*}{n_{so}} = \frac{kT}{q} \ln \left\{ \frac{\eta \phi_o}{n_{so} k_n [A]} + 1 \right\} \qquad (12)$$

predicts a logarithmic dependence of the photogenerated free energy on the illumination intensity (no illumination threshold dependence of ΔG). No formal prediction of this kind is possible according to the Stochastic model, which considers electron transfer as individual events, so invalidating the statistical nature of the photogenerated free energy concept.

II.3. Kinetic Implications of the Quasi-Fermi Level Formalism. *(A) The Regenerative Photoelectrochemical Cell under Applied Bias.* Let us analyze the consequences of applying an external potential bias, V_{cell}, to a regenerative cell, under short-circuit conditions like those shown in Figure 2, where light energy is converted into electricity. In the dark, a cathodic current, J^-, associated with the reduction of A electrolyte species (A + $e_{CB}^- \rightarrow$ A$^-$) flows through the external circuit

$$J^- (cm^{-2} s^{-1}) = (j_c^- + j_v^+) - (j_c^+ + j_v^-) = $$
$$k_n(n_s' - n_{so})[A] + k_p(p_{so} - p_s')[A^-] \quad (13)$$

where j^+ and j^- describe the rates of electron transfer from the electrolyte to the solid and from the solid to the electrolyte, the subindex c and v refers to the conduction and valence band, and n_s' and p_s' are the surface concentration of CB electrons and VB holes, respectively, which are defined by the new Fermi level, E_F', obtained under application of the external potential, V_{cell} ($E_F' - E_{redox} = qV_{cell}$).

Since

$$n_s' = n_{so} \exp\left(\frac{qV_{cell}}{kT}\right) \qquad (14)$$

and

$$p_s' = p_{so} \exp\left(-\frac{qV_{cell}}{kT}\right) \qquad (15)$$
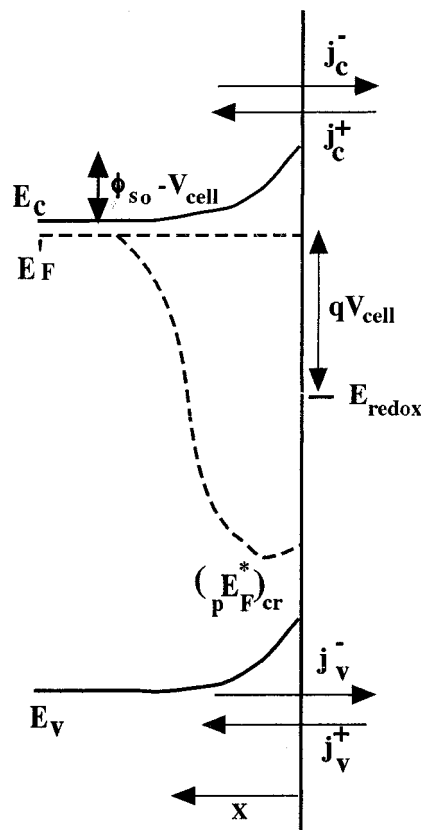

Figure 2. Energy diagram of a regenerative photoelectrochemical cell based on the sc–electrolyte system shown in Figure 1, under application of a negative potential bias, $V_{cell} = (E_F' - E_F/q$, where $E_F = E_{redox}(A^-/A)$. In the dark, a cathodic current, J^-, associated with the reaction A + $e_{CB}^- \rightarrow$ A$^-$, flows through the external circuit. Under illumination, at the steady state, an anodic photocurrent, $J_{ph,st}$, opposed to J^-, which is associated with the photoreaction A$^-$ + $h_{VB}^- \rightarrow$ A, appears. For net photoelectrolysis (net photoproduction of A acceptor from A$^-$ donor species) it must be $J_{ph,st} > J^-$, so that a threshold illumination flux, $(\Phi_o)_{th}$, is required. It must be constated that under open-circuit conditions like those in Figure 1B, for $(\Phi_o) = (\Phi_o)_{th}$ an open-circuit-voltage $V_{oc} = V_{cell}$ should be obtained. Observe that at $x = 0$ $(E_{pF}^*)_{cr}$ reaches the same energy level as in Figure 1B.

it can be assumed that thermal equilibrium in the dark still exists inside the sc, as $n_s' p_s' = n_{so} p_{so} = n_i^2$.

Under illumination, in the absence of surface states able to mediate recombination and/or charge-transfer processes, the interfacial hole flux can be given by an expression similar to (7), where p_{so} is substituted by the actual surface hole concentration in the dark, p_s', so that the stationary photocurrent intensity will be

$$J_{ph,st} = q\eta\phi_o = q\, k_p(p_s^* - p_s')[A^-] \qquad (16)$$

However, only in the case that $J_{ph,st} > q\, J^-$ a net photoproduction of A electrolyte species (net photoelectrolysis) will be possible; by contrast, for $J_{ph,st} < qJ^-$ the production in the dark of A$^-$ species will be dominant.

By equating (13) and (16) the following critical surface hole concentration for net photoproduction of A species is obtained

$$(p_s^*)_{cr} = \frac{k_n}{k_p}(n_s' - n_{so})\frac{[A]}{[A^-]} + p_{so} \qquad (17)$$

Obviously, since the upper limit of $(p_s^*)_{cr}$ is N_V, the value of the
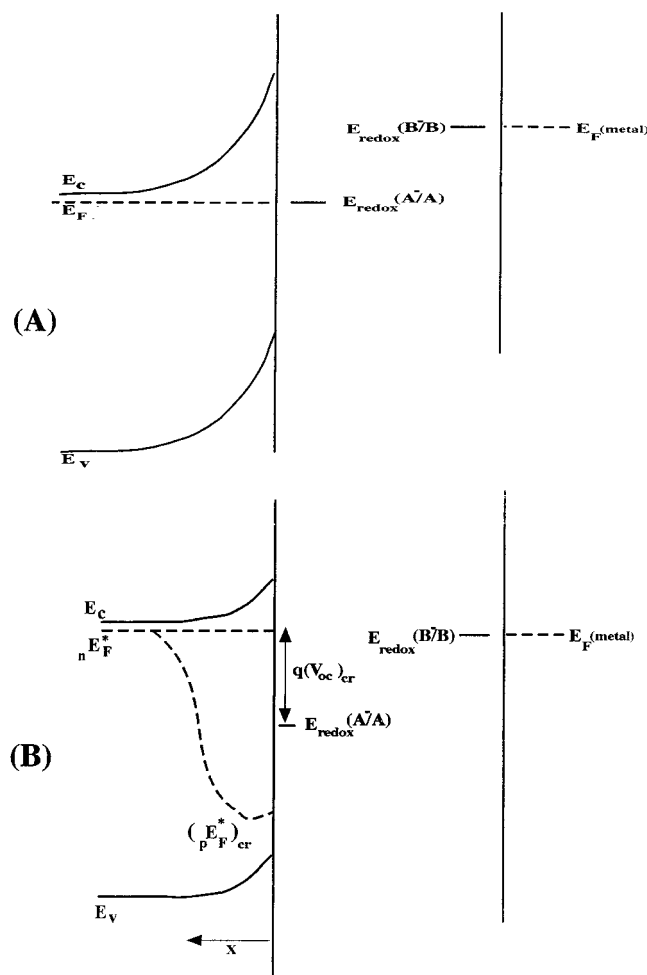
Figure 3. Energy diagram of a photoelectrosynthetic cell under (A) Open-circuit conditions in the dark, where the sc is in equilibrium with the redox couple (A⁻/A) and the metal electrode is in equilibrium with the redox couple (B⁻/B). (B) Short-circuit under threshold illumination conditions. In the dark, the situation is similar to that shown in Figure 2, with $V_{cell} = E_{redox}(B^-/B) - E_{redox}(A^-/A)/q$, so that a cathodic current, J^-, associated with the reduction in the dark of A electrolyte species ($A + e_{CB}^- \rightarrow A^-$) and the simultaneous oxidation of A⁻ species at the metal electrode, flows through the external circuit. An anodic photocurrent, J_{ph}, opposed to J^-, which is associated with the photooxidation of A⁻ species ($A^- + h_{VB}^+ \rightarrow A$), appears under illumination. Net photoelectrolysis ($A^- + B \xrightarrow{h\nu} A + B$) is only obtained for $J_{ph,st} > J^-$, which implies the existence of a threshold illumination flux, $(\Phi_o)_{th}$, able to generate a critical photovoltage ($V_{oc})_{cr} = [E_{redox}(B^-/B) - E_{redox}(A^-/A)/q$. By similitude with Figure 2, at $x = 0$ the critical quasi-Fermi level for holes associated with $(\Phi_o)_{th}$ must be $(E_{pF}^*)_{cr} < E_{redox}(A^-/A)$.

k_n/k_p ratio can in fact constitute a limitation for net photoelectrolysis to be attained when $k_n \gg k_p$ and $n'_s \approx N_V$.

On the other hand, the threshold illumination flux associated with $(p_s^*)_{cr}$ will be

$$(\phi_o)_{th} = \frac{1}{\eta} k_p \{(p_s^*)_{cr} - p'_s\}[A^-] \tag{18}$$

the corresponding critical quasi-Fermi level for holes being

$$(E_{pF}^*)_{cr} = E_V + kT \ln\left(\frac{N_V}{(p_s^*)_{cr}}\right) \tag{19}$$

Since, according to (17), $(p_s^*)_{cr} > p_{so}$ for $\phi_o > 0$, the condition

for net photoproduction of A electrolyte species can be expressed as

$$(E_{pF}^*)_{cr} < E_{redox} \tag{20}$$

Going back to the open-circuit conditions described in Figure 1, the open-circuit voltage to be obtained under an illumination flux $(\phi_o)_{th}$ must be according to (12)

$$(V_{oc})_{cr} = \frac{kT}{q} \ln\left\{ \frac{\eta(\phi_o)_{th}}{n_{so}k_n[A]} + 1 \right\} \tag{21}$$

which, taking into account (14), (15), (17), and (18), becomes

$$(V_{oc})_{cr} = \frac{E'_F - E_{redox}}{q} = V_{cell} \tag{22}$$

Summing up, *the light intensity threshold $\eta(\phi_o)_{th}$ necessary for net photoelectrolysis under application of potential bias V_{cell} (short-circuit conditions in Figure 2) will pruduce in the same system under open-circuit conditions (Figure 1B) an open-circuit voltage $V_{oc} = V_{cell}$.*

(B) *The Photoelectrosynthetic Cell.* In this case, light energy is not only converted into electricity but also into chemical energy (e.g., water photoelectrolysis into H₂ and O₂). As shown in Figure 3A, this type of cell involves two redox couples $E_{redox}(A^-/A)$ and $E_{redox}(B^-/B)$ contained in two isolated compartments. $A^- + h_{VB}^+ \rightarrow A$ is the photooxidation reaction taking place at the sc compartment, while $B + e_{CB}^- \rightarrow B^-$ is the reduction reaction occurring in the dark at the metal compartment, the net reaction being $A^- + B \xrightarrow{h\nu} A + B^-$.

Under open circuit in the dark (Figure 3A), thermodynamic equilibrium is established between both electrodes and the corresponding redox couples, which is expresed as $E_F(sc) = E_{redox}(A^-/A)$ and $E_F(metal) = E_{redox}(B^-/B)$. Under short circuit in the dark, it must be $E_F(metal) = E_F(sc)$, and an electronic flux from the metal to the sc, which is associated with the oxidation of species B⁻ at the metal electrode ($B^- \rightarrow B + e_{metal}^-$) and the simultaneous reduction of A species at the sc ($A + e_{sc}^- \rightarrow A^-$), runs through the external circuit; therefore, the net reaction is $A + B^- \rightarrow A^- + B$. At the sc electrode, the situation is comparable to that of the regenerative cell under external bias (see Figure 2), with $V_{cell} = E_{redox}(B^-/B) - E_{redox}(A^-/A)$. The cathodic current J^- through the external circuit is now described by (13), with

$$n'_s = n_{so} \exp\frac{E_{redox}(B^-/B) - E_{redox}(A^-/A)}{kT}$$

and

$$p'_s = p_{so} \exp\frac{E_{redox}(A^-/A) - E_{redox}(B^-/B)}{kT}$$

n_{so} and p_{so} being the respective equilibrium surface concentrations of CB electrons and VB holes under identical conditions as in Figure 3A (i.e., for $E_F(sc) = E_{redox}(A^-/A)$). On the other hand, under working conditions (i.e., under illumination and with a short circuit, as in Figure 3B) an anodic photocurrent opposed to J^-, $J_{ph,st}$, which is associated with the oxidation of A⁻ species ($A^- + h_{VB}^+ \rightarrow A$), flows through the external circuit

$$J_{ph,st} = q\eta\phi_o = qk_p[A^-](p_s^* - p'_s) \tag{23}$$

It has been claimed that the conventional photoelectrochemical model predicts a light intensity threshold for photoelec-

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trolysis,[5] a prediction which has been subject of controversy for years.[8,9] *Although (23) does not prognosticate an illumination threshold for incipient photoelectrolysis, since $J_{ph,st} > 0$ for $\phi_o > 0$, it predicts a light flux threshold, $(\phi_o)_{th}$, for net photoelectrolysis, such that $J_{ph,st} > qJ^-$ for $\phi_o > (\phi_o)_{th}$.* As in the precedent of case A, the value of the k_n/k_p ratio can constitute a limitation for obtaining net photoelectrolysis, since a $(V_{oc})_{cr} = E_{redox}(B^-/B) - E_{redox}(A^-/A)$ has to be reached (see section II.4.B).

Summing up, the condition for net photoelectrolysis in a photoelectrosynthetic cell is 2-fold; on one hand a critical open-circuit voltage $(V_{oc})_{cr} = E_{redox}(B^-/B) - E_{redox}(A^-/A)/q$ must be reached under open-circuit conditions (Figure 3A), on the other hand it must be $E_{Vs} > (E_{pF}^*)_{cr} < E_{redox}(A^-/A)$, $(V_{oc})_{cr}$, and $(E_{pF}^*)_{cr}$ having the same meaning as in (19) and (21), respectively.

II.4. Thermodynamic Implications of the Quasi-Fermi Level Formalism: Energy Balance and Entropy Loss. The Gibbs equation establishes that in a closed system which can exchange energy but not matter with the outside, under conditions of constant temperature T, volume, and pressure it can be written: $\Delta G = \Delta E - T\Delta S$, i.e., the free energy, ΔG (available energy that can be extracted from the system) is always less than the internal energy ΔE by an entropy term, $T\Delta S$, representing the nonavailable energy (energy lost in vibrations, heat and products that cannot be use for energy conversion). In the case of a photoelectrochemical cell, the increase of internal energy of the photoexcited sc after thermalization of photogenerated carriers must be identified with E_g (the minimum photon energy input to be used in the photoinduced interfacial reaction). Since $\Delta G = qV_{oc}$, it follows that $T\Delta S = E_g - qV_{oc}$.

Again, the following two cases can be distinguished.

(A) *Regenerative Photoelectrochemical Cell.* The energy scheme of Figure 4A refers to a regenerative photoelectrochemical cell under open-circuit conditions and moderate illumination, where $(_pE_F^*)_s = E_{redox}$ (i.e., $p_s^* \approx p_{SO}$), which is equivalent to assume quasi-equilibrium conditions. Therefore, it can be written: $\Delta G = qV_{oc} = (E_{nF}^*)_s - (E)_{pFs}^*$. In this case the entropy term will be

$$T\Delta S = E_g - qV_{oc} = [E_{Cs} - (E_{nF}^*)_s + [(E_{pF}^*)_s - E_{Vs}]] = (T\Delta S)_n + (T\Delta S)_p = (T\Delta S)_{mix} \quad (24)$$

which, taking into account the formal definition of E_{nF}^* and E_{pF}^* in (8) and (9), becomes

$$(T\Delta S)_{mix} = kT \ln\left(\frac{N_C}{n_s^*}\right) + kT \ln\left(\frac{N_V}{p_s^*}\right) = kT \ln\left(\frac{N_C N_V}{n_s^* p_s^*}\right) \approx kT \ln\left(\frac{N_C N_V}{n_s^* p_{so}}\right) \quad (25)$$

In (24) and (25) $(T\Delta S)_{mix}$ is defined as the total entropy of mixing,[17] or the energy to be lost because the concentration of photoexcited states n_s^* and p_s^* only represents a fraction of the concentration of ground states N_C and N_V. $(T\Delta S)_{mix}$ is composed of the mixing entropy term due to VB holes $(T\Delta S)_p$, and that due to CB electrons $(T\Delta S)_n$; $n_s^* p_s^*/N_C N_V$ represents the mole fraction of photogenerated $e^- - h^+$ pairs.[17]

The situation changes when a small enough hole transfer kinetics imposes a surface hole concentration $p_s^* \gg p_{so}$, such that $qV_{oc} = (E_{nF}^*)_s - E_{redox} \ll (E_{nF}^*)_s - (E_{pF}^*)_s$, which is equivalent to assume that equilibrium conditions are broken
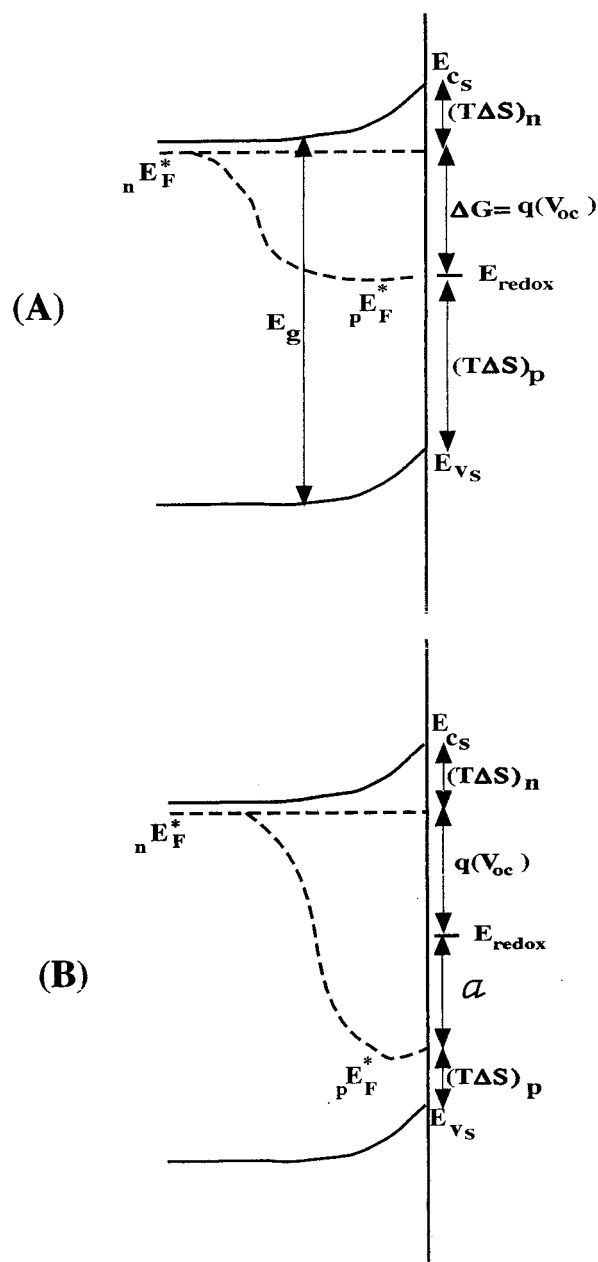
Figure 4. Energy balance scheme of the regenerative photoelectrochemical cell shown in Figure 2, under open-circuit and illumination conditions, for (A) Rapid interfacial hole transfer such that $p_s^* \approx p_{so}$ (quasi-equilibrium conditions). (B) Slow interfacial hole transfer, such that $p_s^* \gg p_{so}$ (nonequilibrium conditions). According to Gibbs equation, under conditions of constant temperature, T, volume, and pressure, it is $\Delta G = \Delta E - T\Delta S$, where the internal energy increase of the photoexcited sc, ΔE, is identifiable with the band gap, E_g (the minimum photon energy input to be used in the photoinduced interfacial reaction), ΔG is the Gibbs energy or the available photogenerated energy (i.e., $\Delta G = qV_{oc}$), and $T\Delta S$ represents the entropy loss (nonavailable energy). Case A assumes near equilibrium conditions, where $\Delta G = (E_{nF}^*)_s - (E_{pF}^*)_s$ and $(T\Delta S)_{mix} = (T\Delta S)_n + (T\Delta S)_p$ represents the mixing entropy, or the energy to be lost because the concentration of photoexcited states, n_s^* and p_s^*, only represents a fraction of the surface concentration of ground states, N_C and N_V (see (24) and (25)); $(T\Delta S)_n$ and $(T\Delta S)_p$ are defined as the mixing entropy for electrons and holes, respectively. By contrast, in case B, where conditions far for equilibrium are assumed, a new entropy term, a $= E_{redox} - E_{pF}^*$, appears to compensate the diminution of $(T\Delta S)_p$, so that $T\Delta S = a + (T\Delta S)_{mix}$.

under illumination (Figure 4B). In this case the term $(T\Delta S)_p = kT \ln N_V/p_s^*$ experiments a decrease, a new entropy term $a =$

$E_{\text{redox}} - (E_{\text{pF}}^*)_s$ appearing to compensate this diminution, so that $(T\Delta S)_p + a = E_{\text{redox}} - E_{Vs}$ and (24) becomes

$$T\Delta S = (T\Delta S)_n + (T\Delta S)_p + a =$$
$$kT \ln\left(\frac{N_C}{n_s^*}\right) + kT \ln\left(\frac{N_V}{p_s^*}\right) + kT \ln\left(\frac{p_s^*}{p_{so}}\right) \quad (26)$$

Finally, (26) can be written

$$T\Delta S = (T\Delta S)_{\text{mix}} + a \quad (27)$$

As will be shown below, the term a, which like V_{oc} depends logarithmically on ϕ_o, has to be identified with the entropy loss associated with photoinduced interfacial charge transfer ($A^- + h_{VB}^+ \rightarrow A$ for the case of a n-type sc).

(B) *Photoelectrosynthetic Cell.* As we have seen in section II.3.B, the minimum photogenerated free energy required for net photoelectrolysis in a photoelectrosynthetic cell must equal the free energy involved in the net endoergic electrolyte reaction, $\Delta G = E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)$. This implies the existence of a threshold illumination flux, $(\Phi_o)_{\text{th}}$, able to generate a critical open-circuit voltage, $(V_{\text{oc}})_{\text{cr}} = \Delta G/q = E_{\text{redox}}B^-/B) - E_{\text{redox}}(A^-/A)/q$. Under open-circuit conditions, in the absence of surface recombination, the hole flux crossing the interface under threshold illumination will be $\eta(\Phi_o)_{\text{th}} = k_p[A^-][(p_s^*)_{\text{cr}} - p_{so})]$. The steady state will be reached when $\eta(\Phi_o)_{\text{th}} = k_p[(p_s^*)_{\text{cr}} - p_{so})][A^-] = k_n[(n_s^* - n_{so})[A]$, which, taking into account the definition of a and qV_{oc}, becomes

$$\eta(\Phi_o)_{\text{th}} = n_{so}k_n[B]\left\{\exp\left(\frac{E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)}{kT}\right) - 1\right\} =$$
$$p_{so}k_p[A^-]\left\{\exp\left(\frac{a_{\text{cr}}}{kT}\right) - 1\right\} \quad (28)$$

where a_{cr} is the critical entropy loss associated with $\eta(\Phi_o)_{\text{th}}$. The diagram of Figure 5 shows the energy balance of the photoelectrosynthetic cell under short-circuit conditions and threshold illumination. In this case

$$E_{\text{nF}}^* - E_{\text{pF}}^* = [E_{\text{redox}}(B^-/B)) - E_{\text{redox}}(A^-/A)] + a_{\text{cr}} =$$
$$q(V_{\text{oc}})_{\text{cr}} + a_{\text{cr}} \quad (29)$$

and

$$E_g = (T\Delta S)_n + (T\Delta S)_p =$$
$$a_{\text{cr}} + [E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)] =$$
$$T\Delta S + q(V_{\text{oc}})_{\text{cr}} \quad (30)$$

The entropy term $a_{\text{cr}} + (T\Delta S)_p = E_{\text{redox}}(A^-/A) - E_{Vs}$ is known as the intrinsic overpotential of the sc anode η_a, and η_c as the overpotential of the metal electrode.[5] Since $(T\Delta S)_n = E_{Cs} - E_{\text{nF}}^* = \phi_s + \Delta E_F$, (30) can be written as

$$E_g = q(V_{\text{oc}})_{\text{cr}} + \eta_a + \eta_c + \phi_s + \Delta E_F \quad (31)$$

Therefore, it can be inferred that the entropy of mixing for electrons, $(T\Delta S)_n$, is associated with the energy loss of photogenerated carriers due to the space charge region drift. As for the term $E_g - \phi_s - \Delta E_F$, it can be identified with the potential energy of photogenerated e^-–h^+ pairs. A fraction of this potential energy is recovered as free energy of the net endoergic reaction in the electrolyte ($\Delta G = E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)$), the remaining potential energy being lost through the

Figure 5. Energy balance scheme of the photoelectrosynthetic cell shown in Figure 3, under short-circuit and threshold illumination conditions, so that $(qV_{\text{oc}})_{\text{cr}} = E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)$ (free energy involved in the net endoergic electrolyte reaction). a_{cr} represents the critical entropy due to the photoelectrochemical reaction, which is associated with the threshold illumination flux, $(\Phi_o)_{\text{th}}$ (see (28)). The irreversible, entropy producing term $\eta_a = a + (T\Delta S)_p$ is known as the intrinsic overpotential of the sc electrode, while η_c represents the overpotential of the metal electrode. The energy balance becomes $E_g = (qV_{\text{oc}})_{\text{cr}} + \eta_a + \eta_c + (T\Delta S)_n = (qV_{\text{oc}})_{\text{cr}} + T\Delta S$. Observe that the mixing entropy term due to electrons, $(T\Delta S)_n = \phi_s + \Delta E_F$ is associated with the bandbending ϕ_s and, therefore, is related to the energy lost by photogenerated charge carriers when traversing the interfacial electric field region.

irreversible entropy producing term $\eta_a = a_{\text{cr}} + (T\Delta S)_p$. It is worthwhile to observe that the bandbending ϕ_s is necessary for an efficient e^-–h^+ separation. In the case that the energy difference $E_{Cs} - E_{\text{redox}}(B^-/B)$ is not high enough for sustaining a convenient ϕ_s, as in the case for water photoelectrolysis at TiO_2 electrodes, ϕ_s can be increased by applying an external anodic bias to the cell.[5]

Summing up, as for the case of the regenerative cell, the requirement for net photoelectrolysis in a photoelectrosynthetic cell is 2-fold: on one hand it must be $q(V_{\text{oc}})_{\text{cr}} > E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)$ (free energy of the net electrolyte reaction), on the other hand, the condition $E_{Vs} < (E_{\text{pF}}^*)_{\text{cr}} < E_{\text{redox}}(A^-/A)$ now becomes $a_{\text{cr}} \leq \eta_a$. It could happen that, due to a relatively low hole transfer rate constant, k_p, the surface concentration of photogenerated holes may reach saturation (i.e., $p_s^* \approx N_V$) for an illumination flux lower than $(\Phi_o)_{\text{th}}$. In this case, $q(V_{\text{oc}})_{\text{cr}}$ would be lower than $E_{\text{redox}}(B^-/B) - E_{\text{redox}}(A^-/A)$ and net photoelectrolysis would not be possible.

A more precise physical meaning of the entropy term, σ is beyond the possibilities of equilibrium thermodynamics. Since a defines the deviation from equilibrium of the surface concentration of photogenerated holes, a nonequilibrium concept which fall within the domain of nonequilibrium thermodynamics, this branch of thermodynamics is expected to be an interesting tool for a further study of irreversible, light assisted reactions in fuel-forming photoelectrochemical systems.

III. The Nonequilibrium Thermodynamic Approach

III.1. The Principles. Nonequilibrium thermodynamics constitutes a macroscopic theory of irreversible processes, therefore

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adequate for describing photoelectrochemical reactions. This theory has a double foundation: on one hand, the Onsager reciprocity relations,[18] which are macroscopic equalities built up upon the basis of the microscopic reversibility principle, on the other hand, the introduction of nonequilibrium thermodynamic concepts, like entropy production, not present in Gerischer's model, which are necessary for a correct formulation of the entropy balance equation. As we will show along this section, the nonequilibrium thermodynamic approach allows to formulate for the first time a dependence between the mechanism of transfer of charge at the illuminated sc−electrolyte interface and the physical magnitudes thermodynamicaly deffining the irreversible photoelectrochemical system

There are a great number of phenomenological laws describing irreversible processes as proportionality relationships between thermodynamic forces, X_k (e.g., concentration gradient, chemical affinity, etc.) and conjugated fluxes, J_i (e.g., velocity of diffusion, reaction rate, etc.). Some examples are the Fick law, which relates the flux of matter with the concentration gradient and the law of chemical reactions, linking the reaction rate with the chemical potential.

Let us consider a reactive system of n constituents ($x_i x_n$) participating in r chemical reactions, and let ω_ρ ($\rho = 1...r$) be their individual reaction rates.per volume unit In nonequilibrium thermodynamics, a thermodynamic state is defined by certain state parameters (composition variables) $\rho_1...\rho_n$ which deviation from equilibrium constitutes the state variables $\alpha_i = \rho_i - \rho_i^o$, with ρ_i^o defining the equilibrium value of the parameter ρ_i.

The entropy S of a nonequilibrium state is defined as a functional depending not only on the parameters ρ_i but on their gradient in space and variation with time[19]

$$S = S\left(\rho_i; \nabla\rho_i; \ \frac{\delta\rho_i}{\delta t}\right) \tag{32}$$

Therefore, S becomes an implicit function of time through the parameters ρ_i.

By defining the entropy density S_v, such that $S = \int S_v \, dV$, it can be shown[18] that in a closed system which can exchange energy but not matter with the surroundings,

$$\frac{\delta S_v}{\delta t} = \sum_\rho\left[-\sum_i \frac{\mu_i}{T}\nu_{i\rho}\right]\omega_\rho - \sum_i j_i \nabla\frac{\mu_i}{T} = \sum_\rho \frac{a_\rho}{T}\omega_\rho - \sum_i j_i \nabla\frac{\mu_i}{T} \tag{33}$$

where μ_i, j_i, and $\nu_{i\rho}$ represent the chemical potential, the diffusion flux and the stoichiometric coefficient of constituent x_i, respectively, and $a_\rho = -\sum_i \mu_i \nu_{i\rho}$ defines the affinity of reaction ρ. Since at equilibrium $a_\rho = 0$, the affinity measures the deviation of a chemical reaction from its equilibrium state. Equation 33 is a particular case of Gibbs equation under nonequilibrium conditions.

Finally, the entropy production of a thermodynamic system can be written as[18]

$$\sigma = \frac{\delta S_v}{\delta t} = -\sum_i j_i \nabla\frac{\mu_i}{T} + \sum_\rho \frac{{}^a\rho}{T}\omega_\rho = \sum_i X_i J_i \tag{34}$$

Equation 34 expresses the entropy balance as a bilinear form of the magnitudes j_i and ω_ρ, which can be seen as the flows J_i, associated with the various irreversible processes, and of the quantities $\nabla\mu_i/T$ and a_ρ/T representing the corresponding generalized forces, X_i. While $\sigma > 0$ for any entropy producing,

irreversible process, for a reversible process connecting two equilibrium states is $\sigma = 0$.

Near equilibrium, when the generalized forces X_i remains sufficiently weak, the flow J_i can be approached by a Taylor series of X_i written up to the second term, which yields to the following phenomenological relationship between fluxes and forces[19]

$$J_i = \sum_k L_{ik}X_k \tag{35}$$

where $L_{ik} = \partial J_i/\partial X_k$ are phenomenological coefficients entirely determined by the internal structure of the medium. Equation 35 defines the linear range of an irreversible process where according to Onsager theorem, the matrix of phenomenological coefficients must be symmetric (i.e., $L_{ik} = L_{ki}$) under adequate election of fluxes and forces.[19] These identities, known as Onsager reciprocity relations, express the relationship between reciprocal phenomena arising from the mutual interference between irreversible processes that occur simultaneously (e.g., thermic and electric conduction and diffusion flux). They are rigorous consequences or the property of detailed balance or, alternatively, of the time-reversal invariance of the elementary steps associated with the irreversible phenomena.

III.2. **The Photoelectrochemical Cell as an Irreversible System.** The phenomenological theory of electrical transport effects in semiconductors from an irreversible thermodynamics point of view was treated by Tauc.[20] According to this author, the Onsager system in a sc is composed by three kind of currents (fluxes): an electric current of density J_n, a particle current of density J_N, and a thermal current of density J_q. The corresponding conjugated forces are

$$X_n = \nabla\Phi \tag{36}$$

$$X_N = \nabla\frac{\mu_n}{T} \tag{37}$$

and

$$X_q = -\frac{1}{T}\nabla T \tag{38}$$

where Φ is the electric potential, μ_n represents the chemical potential for electrons, and T is the lattice temperature. According to (35) we can write:

$$J_n = L_{11}\left(-q\nabla\Phi + T\nabla\frac{\mu_n}{T}\right) + L_{12}\frac{1}{T}\nabla T \tag{39}$$

$$J_q = L_{21}\left(-q\nabla\Phi + T\nabla\frac{\mu_n}{T}\right) + L_{22}\frac{1}{T}\nabla T \tag{40}$$

where according to Onsager,[18] $L_{12} = L_{21}$, $L_{11} = \sigma_n/q$, and $L_{22} = -\kappa_n/T$, σ_n and κ_n being the electrical and thermal conductivity, respectively. Moreover,

$$\frac{L_{21}}{L_{11}} = \frac{L_{21}}{L_{11}} = \frac{I_n}{I_q} = Q_n^* \tag{41}$$

where the quantity Q_n^* stands for the termal current density corresponding to the unit density of the electron current for $T = 0$.

For constant lattice temperature (39) is equivalent to the well-known Shockley equation,[13]

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$$J_n = q[D_n \nabla n^* - \mu n^* \nabla \Phi] = -q\mu n^* \nabla E_{nF}^* \quad (42)$$

which demonstrates the compatibility between the quasi-Fermi level formalism and nonequilibrium thermodynamics.

Equation 42 represents the phenomenological reletionship between the thermodynamic force ∇E_{nF}^* and the conjugated electron flux J_n. A similar expression can be obtained for the current of VB holes[13]

$$J_p = q[D_p \nabla p^* - \mu p^* \nabla \Phi] = -q\mu p^* \nabla E_{pF}^* \quad (43)$$

III.3. Energetics of a Photoelectrochemical Reaction: The Photoelectrochemical Affinity.

Let us consider a simple photoassisted electrochemical reaction $(h_{VB}^+ + A^- \xrightarrow{k_p} A)$ taking place at the n-type sc−electrolyte interface. Since the concentration of electrolyte species can be considered to be unaffected under illumination, the only state variable of this system will be $\alpha_i = p_s^* - p_{so} = \Delta p_s$. Taking into account the kinetic description of the photoinduced, interfacial charge-transfer process given in section II ((5)−(7)), (33) allows to describe the affinity of the photoelectrochemical reaction, in the following "photoelectrochemical affinity", as

$$a_{ph} = kT \ln \frac{k p_{ps}^*[A^-]}{k_p^{-1}[A]} = kT \ln \frac{k p_{ps}^*[A^-]}{k_p p_{so}[A^-]} = kT \ln \frac{p_s^*}{p_{so}} \quad (44)$$

In the absence of surface recombination, the interfacial reaction rate per volume unit ω_ρ can be identified with the photocurrent intensity:

$$\omega_\rho = \frac{1}{d} \frac{J_{ph}}{q} = \frac{1}{d}(k p_{ps}^*[A^-] - k_p^{-1}[A]) = \frac{1}{d} k_p[A^-](p_s^* - p_{so}) \quad (45)$$

where $d \approx 10^{-8}$cm represents the reaction layer thickness. By combining (44) and (45), the following relationship between the photoelectrochemical affinity (thermodynamic force) and the photocurrent (conjugated flux) is obtained:

$$J_{ph} = q k_p p_{so}[A^-]\left[\exp\left(\frac{a_{ph}}{kT}\right) - 1\right] \quad (46)$$

Equation 45 defines the nonlinear range of the irreversible photoelectrochemical reaction. The corresponding linear range (see (35)) refers to a situation very near equilibrium, where $a_{ph} \ll kT$ (i.e., $p_s^* \approx p_{so}$), so that (46) becomes

$$J_{ph} = q k_p p_{so}[A^-] \frac{a_{ph}}{kT} \quad (47)$$

Obviously, the condition that $a_{ph} \to 0$ in the linear range necessarily implies that $k_p \to \infty$ (i.e., equilibrium conditions are approached).

On the other hand, taking into account the formal definition of E_{pF}^*, (44) becomes

$$a_{ph} = E_{redox} - (E_{pF}^*)_s \quad (48)$$

According to (48), the quasi-Fermi level for VB holes at the sc surface represents a measurement of the deviation of the system under illumination with respect to the equilibrium in the dark. Moreover, since $qV_{oc} = (E_{nF}^*)_s - E_{redox}$, we arrive at the conclusion that

$$(E_{nF}^* - E_{pF}^*) = a_{ph} + qV_{oc} \quad (49)$$

Obviously, only very near equilibrium, for $a_{ph} \approx 0$, we can say that $qV_{oc} = (E_{nF}^*)_s - (E_{nF}^*)_s$, as expressed by (10).

By comparing (48) with (26), *it can be concluded that the entropy term, a, of model A, appearing in (26), must be identified with the photoelectrochemical affinity, a_{ph}, of the irreversible photoreaction in model C.* Therefore, the total entropy loss defined by (27) becomes

$$T\Delta S = (T\Delta S)_{mix} + a_{ph} \quad (50)$$

a_{ph} representing the entropy loss due to irreversibility of the photoinduced charge-transfer process between the VB and the electrolyte.

It is worth while to go further into the existing relationship between a_{ph} and qV_{oc}. Under open-circuit conditions, as in Figure 4B, and in the absence of surface recombination, by analogy with (28) we can write

$$\eta\Phi_o = n_{so}k_n[A]\left\{\exp\left(\frac{qV_{oc}}{kT}\right) - 1\right\} =$$
$$p_{so}k_p[A^-]\left\{\exp\left(\frac{a_{ph}}{kT}\right) - 1\right\} \quad (51)$$

from which we obtain

$$a_{ph} = kT \ln\left(\frac{\eta\phi_o}{k_p p_{so}[A^-]} + 1\right) \quad (52)$$

Like (12) with respect to V_{oc}, (52) predicts a logarithmic dependence of the photoelectrochemical affinity on the photon flux, but not an illumination threshold, as $a_{ph} > 0$ for $\Phi_o > 0$. Moreover, (52) establishes an explicit relationship between a_{ph} and the hole transfer rate constant k_p, in the same way as (12) links the sc photogenerated free energy, qV_{oc}, with the CB electron-transfer rate constant, k_n.

Rearranging (51), we obtain

$$\frac{n_{so}k_n[A]}{p_{so}k_p[A^-]} = \frac{\exp\left(\frac{a_{ph}}{kT}\right) - 1}{\exp\left(\frac{qV_{oc}}{kT}\right) - 1} \equiv B \text{ (constant)}$$

which, for the case of high enough illumination intensity (i.e., for $n_{so}k_n[A] \ll \eta\phi_o \gg p_{so}k_p[A^-]$), such that $qV_{oc} \geq 4kT \leq a_{ph}$, becomes $B \approx \exp(a_{ph} - qV_{oc}/kT)$, which leads to the important conclusion that

$$a_{ph}\text{-}qV_{oc} = kT \ln\left(\frac{n_{so}k_n[A]}{p_{so}k_p[A^-]}\right) = \text{const} \quad (53)$$

In the particular case of a photoelectrosynthetic cell, *(53) establishes a formal relationship between a_{ph} (the thermodynamic driving force of the photoelectrochemical reaction) and the free energy stored.* In fact, according to section II.3.B, an illumination threshold $(\Phi_o)_{th}$ able to produce a critical photovoltage $(V_{oc})_{cr} = [E_{redox}(B^-/B) - E_{redox}(A^-/A)]/q$, is required for net photoelectrolysis. According to (53), he critical photoelectrochemical affinity associated with $(\Phi_o)_{th}$ will be

$$(a_{ph})_{cr} = kT \ln\left(\frac{n_{so}k_n[A]}{p_{so}k_p[A^-]}\right) + (qV_{oc})_{cr}$$

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Moreover, *(53) establishes a clear relationship between a_{ph} and qV_{oc} through the kinetic factors (charge-transfer rate constants, k_n and k_p).*

From a practical point of view, the following question can be proposed: may any experimentally observable difference distinguish between the illuminated sc-liquid junction operating under the equilibrium rather than under the nonequilibrium model? The answer is positive, a main difference exists, which concerns the maximum photogenerated free energy (V_{oc})$_{max}$, to be stored by the system. While the equilibrium model predicts a $(V_{oc})_{max} \approx E_{Cs} - E_{redox}$ which is independent of the interfacial charge-transfer kinetics, for the nonequilibrium model the influence of kinetic factors on $(V_{oc})_{max}$, like the k_n/k_p ratio, is evident. To this respect, it must be emphasized that the type of sc−electrolyte interaction plays an important role. In fact, two main cases can be distinguished:

(A) Weak SC−Electrolyte Interaction. According to the Marcus−Gerischer model for weak interaction, the rate constant for isoenergetic electron transfer can be approximated by the expression[15]

$$k_n = \sigma'_n d\bar{c} \left(\frac{kT}{\pi\lambda}\right)^{1/2} \exp\left\{-\frac{[E_{cS} - (E_{redox} + \lambda)]^2}{4\lambda kT}\right\} \quad (54)$$

where σ'_n is the cross section for electron capture of oxidized electrolyte species, $\bar{c}$ is the average thermal velocity of CB electrons, d is the reaction length, and λ is the reorganization energy of the (A^-/A) redox couple. By analogy, it can be written

$$k_p = \sigma'_p d\bar{c} \left(\frac{kT}{\pi\lambda}\right)^{1/2} \exp\left(-\frac{[(E_{redox} - \lambda) - E_{vs}]^2}{4\lambda kT}\right) \quad (55)$$

where σ'_p is the cross section for hole capture of reduced electrolyte species; therefore,

$$\ln \frac{k_n}{k_p} = \ln \frac{\sigma'_n}{\sigma'_p} + \frac{E_g^2 - 2E_g[(E_{Cs} - E_{redox}) + \lambda] + 4(E_{Cs} - E_{redox})\lambda}{4\lambda kT} \quad (56)$$

On the other hand,

$$\ln \frac{n_{so}}{p_{so}} = \ln \frac{N_C}{N_V} + \frac{2(E_{redox} - E_{Vs}) - E_g}{kT} \quad (57)$$

so that

$$\ln B = \ln \frac{N_C}{N_V} + \frac{2(E_{redox} - E_{Vs}) - E_g}{kT} +$$
$$\frac{E_g^2 - 2E_g[(E_{Cs} - E_{redox}) + \lambda] + 4(E_{Cs} - E_{redox})\lambda}{4\lambda kT} +$$
$$\ln \frac{[A^-]}{[A]} + \ln \frac{\sigma'_n}{\sigma'_p} \quad (58)$$

which can be simplified in the case that $[A] = [A^-]$ and $N_c \approx N_v$, becoming

$$\ln B = \frac{E_g - 2(E_{Cs} - E_{redox})}{kT} +$$
$$\frac{E_g^2 - 2E_g[(E_{Cs} - E_{redox}) + \lambda] + 4(E_{Cs} - E_{redox})\lambda}{4\lambda kT} + \ln \frac{\sigma'_n}{\sigma'_p} \quad (59)$$

Then (53) can be written as

$$a_{ph}\text{-}qV_{oc} \approx \frac{E_g - 2(E_{Cs} - E_{redox})}{kT} +$$
$$\frac{E_g^2 - 2E_g[(E_{Cs} - E_{redox}) + \lambda] + 4(E_{Cs} - E_{redox})\lambda}{4\lambda kT} + \ln \frac{\sigma'_n}{\sigma'_p} \quad (60)$$

which is valid for any photon flux. For the special case that $\sigma'_n \approx \sigma'_p$ and $E_{Cs} - E_{redox} = E_g/2$ it is $a_{ph} \approx qV_{oc}$.

Let $(\phi_o)_{cr,1}$ be the critical photon flux at which E^*_{pF} reaches a value near E_{Vs} (i.e., for $p^*_s \approx N_V$), so that the photoelectrochemical affinity reaches its theoretical, maximum allowed value, $(a_{ph})_{max} \approx E_{redox} - E_{Vs}$ (Figure 6A). On the other hand, let $(\phi_o)_{cr,2}$ be the critical photon flux at which the open−circuit voltage reaches its theoretical, maximum allowed value, $(V_{oc})_{max} = (E_{Cs} - E_{redox}) - \Delta E_F/q$. In the absence of entropy loss due to irreversibility (i.e., under quasi-equilibrium conditions where $p^*_s \approx p_{so}$), $(\phi_o)_{cr,2}$ is defined by (12), where k_n is the only intervening kinetic parameter (for the sake of simplicity we assume that in (12) η does not depend on the photon flux, which is equivalent to admit bandbending independent bulk recombination). However, due to the entropy loss associated with the irreversible hole transfer reaction, which is defined by a_{ph}, the maximum actual value of V_{oc} will be lower than the theoretical $(V_{oc})_{max}$, only being $V_{oc}=(V_{oc})_{max}$ in the case that $(\phi_o)_{cr,1} \geq (\phi_o)_{cr,2}$. Taking into account (12) and (51), this condition can be expressed as

$$k_n n_{so}[A]\left\{\exp\left(\frac{E_{Cs} - E_{redox} - \Delta E_F}{kT}\right) - 1\right\} \leq$$
$$p_{so}k_p[A^-]\left\{\exp\left(\frac{E_{redox} - E_{Vs}}{kT}\right) - 1\right\} \quad (61)$$

which becomes

$$kT \ln B \leq E_g - 2(E_{Cs} - E_{redox}) + \Delta E_F \quad (62)$$

For simplification, it can be assumed that $[A] = [A^-]$ and $N_C = N_V$; then, with the help of (59), (62) becomes

$$\ln \frac{\sigma'_n}{\sigma'_p} \leq \frac{\Delta E_F}{kT} - \frac{E_g^2 - 2E_g[(E_{Cs} - E_{redox}) + \lambda] + 4(E_{Cs} - E_{redox})\lambda}{4\lambda kT} \quad (63)$$

Equation 63 translates into a kinetic language the requirement for the system to be able to reach the theoretical, maximum allowed photogenerated free energy, $\Delta G_{max} = E_{Cs} - E_{redox} - \Delta E_F$, when the entropy loss due to irreversibility is taken into account. Figure 6 illustrates the influence of a_{ph} on the actual, maximum attainable open-circuit voltage for the ideal case of a bandbending independent quantum efficiency.

The requirement expressed by (55) also applies to a photoelectrosynthetic cell (see section II.4.B). In this case, $(\phi_o)_{cr,2}$ must be identified with the threshold illumination flux able to
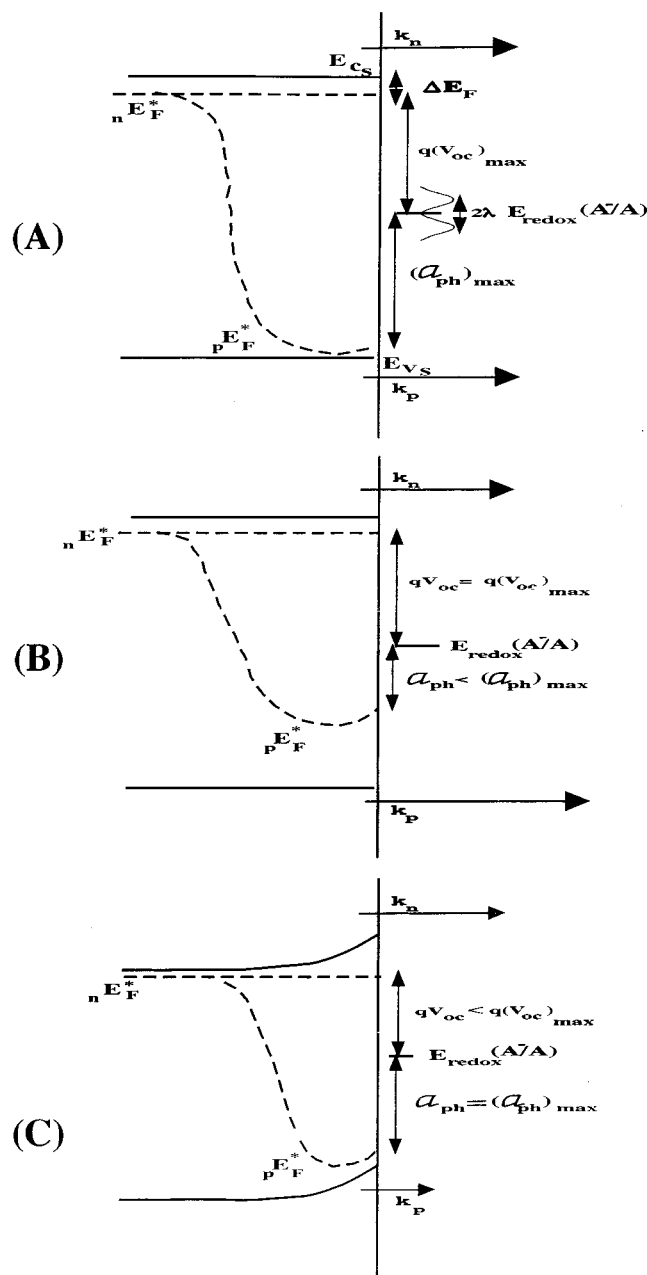
Figure 6. Energy balance scheme for a weak electronic interaction, illuminated sc—electrolyte system based on the Marcus—Gerischer model, under short-circuit conditions, where according to (52), for any photon flux, $a_{ph} - qV_{oc}$ not only depends on the energy position of the redox couple (i.e., $E_{Cs} - E_{redox}$), E_g and λ, but also on the ratio of cross sections for CB electrons and VB holes for capture by electrolyte species, σ'_n/σ'_p. Three different cases are considered where a unique n-type sc of band gap E_g interacts with three electrolytes of identical ($E_{Cs} - E_{redox} = E_g/2$), and where λ and k_n are maintained invariable while k_p is considered to change ($k_p(B) > k_p(A) > k_p(C)$). Equations 54 and 55 establish the conditions for the system being able to reach the theoretical, maximum allowed photogenerated free energy, $\Delta G_{max} = E_{Cs} - E_{redox} - \Delta E_F$, ΔE_F being defined in Figure 5. (A) Illustrates the case where $k_n \approx k_p$ and $\phi_o \approx (\phi_o)_{cr,1} \approx (\phi_o)_{cr,2}$, so that $qV_{oc} + a_{ph} \approx (qV_{oc})_{max} + (a_{ph})_{max} \approx E_g - \Delta E_F$. In case B is $k_n < k_p$ and $\phi_o = (\phi_o)_{cr,2} < (\phi_o)_{cr,1}$, so that $qV_{oc} < (qV_{oc})_{max}$ and $a_{ph} = (a_{ph})_{max}$. (C) Illustrates the case where $k_n > k_p$ and $\phi_o = (\phi_o)_{cr,1} < (\phi_o)_{cr,2}$, so that $qV_{oc} < (qV_{oc})_{max}$ and $a_{ph} = (a_{ph})_{max}$. (($\phi_o)_{cr,1}$ and $(\phi_o)_{cr,2}$ represents the theoretical, critical photon flux at which $a_{ph} = (a_{ph})_{max}$ and $qV_{oc} = (qV_{oc})_{max}$, respectively; while $(\phi_o)_{cr,2}$ remains constant, $(\phi_o)_{cr,1}$ varies with k_p, in such a way that $\phi_o(A) = \phi_o(B) > \phi_o(C)$; an ideally, bandbending independent quantum efficiency is considered in all cases).

photogenerate a free energy, $\Delta G = E_{redox}(B^-/B) - E_{redox}(A^-/A)$ (see section VI.2)

$$(\phi_o)_{cr,2} =$$

$$\frac{1}{\eta} k_n n_{so}[A] \left\{ \exp\left(\frac{E_{redox}(B^-/B) - E_{redox}(A^-/A)}{kT} \right) - 1 \right\}$$

while the critical photon flux at which $a_{ph} = (a_{ph})_{max} = E_{redox}(A^-/A) - E_{Vs}$ will be

$$(\phi_o)_{cr,1} = \frac{1}{\eta} k_p p_{so}[A^-] \left\{ \exp\left(\frac{E_{redox}(A^-/A) - E_{Vs}}{kT} \right) - 1 \right\}$$

with n_{so} and p_{so} defined by the equilibrium conditions of Figure 3A. Therefore, the condition for net photoelectrolysis has to be

$$B = \frac{n_{so}k_n[A]}{p_{so}k_p[A^-]} \leq$$

$$\exp\left(\frac{[E_{redox}(B^-/B) - E_{redox}(A^-/A)] - [E_{redox}(A^-/A) - E_{Vs}]}{kT} \right)$$

$$(64)$$

with B given by (59).

(B) Strong SC—Electrolyte Interaction. In this case electrolyte species can be considered to behave like band gap surface states, so that a process of inelastic photoinjection of holes into adsorbed electrolyte species without necessity of tunneling can be envisaged[20] (Marcus—Gerischer model is no longer applied). The exponential term involved in the rate transfer constants k_n and k_p ((54) and (55)) therefore disappears,[21,22] becoming $k_n = \bar{c}\sigma'_n$ and $\bar{c}\sigma'_p$, so that according to (53) and (59) it is

$$\ln B = \frac{E_g - 2(E_{Cs} - E_{redox})}{kT} + \ln\frac{\sigma'_n}{\sigma'_p}$$

and

$$a_{ph}\text{-}qV_{oc} = E_g - 2(E_{Cs} - E_{redox}) + kT\ln\frac{\sigma'_n}{\sigma'_p} \qquad (65)$$

Therefore, according to (62), the requirement for the system being able to reach the theoretical, maximum allowed photogenerated free energy (i.e., $\Delta G_{max} = E_{Cs} - E_{redox} - \Delta E_F$) can be expressed in this case as

$$\frac{\sigma'_n}{\sigma'_p} \leq \exp\frac{\Delta E_F}{kT} \qquad (66)$$

III.4. Entropy Production of a Photoelectrochemical Cell. Finally, let us determine the entropy production of the irreversible photoelectrochemical reaction involved in the energy balance expresion (33). The total generated entropy consisits in two terms, the entropy generated by CB electrons, σ_n, and that produced by photogenerated VB holes, $\sigma_p (\sigma = \sigma_n + \sigma_p)$. According to (34) both entropy terms must be expressed in the following way:

$$\sigma_n = \Sigma J_n X_n \qquad (67)$$

and

$$\sigma_p = \Sigma J_p X_p \qquad (68)$$

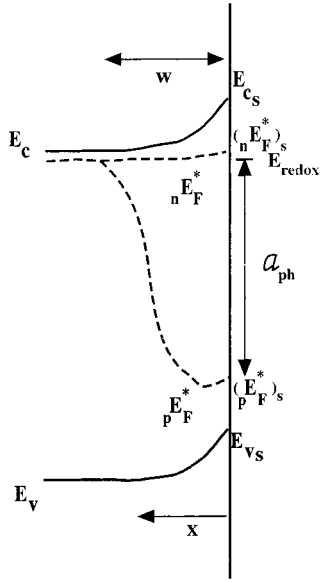where J_n and J_p represents de flux of electrons and holes,

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can write

$$\langle\sigma\rangle = \langle\sigma_n\rangle + \langle\sigma_p\rangle = \frac{1}{T}\frac{J_{ph,st}}{q}\frac{[(E_{nF}^*)_s - E_{redox}^o] + a_{ph}}{W}$$

As can be seen in Figure 7, which illustrates the case of a regenerative photoelectrchemical cell based on a n-type sc photoelectrode where $E_{Cs} - E_{redox}^o < E_{redox}^o - E_{Vs}$, it is $n_s^* \approx n_{so}$ and $p_s^* \gg p_{so}$, so that $a_{ph} \gg E_{Cs} - E_{redox}^o$, becoming $\langle\sigma_n\rangle$ negligible vs $\langle\sigma_p\rangle$; therefore, we can write

$$\langle\sigma\rangle \approx \langle\sigma_p\rangle = \frac{1}{W}\frac{J_{ph,st}}{q}\frac{a_{ph}}{T} \quad (71)$$

On one hand, (71) shows us that entropy will be continuously generated by the photoelectrochemical system as far as the photocurrent is different from zero, the entropy production rate being proportional to the photoelectrochemical affinity a_{ph}, which is controlled by the hole transfer rate constant k_p, according to (52). In the limit case that $k_p \approx \infty$, corresponding to quasi-equilibrium conditions, will be $a_{ph} = 0$ and no entropy will be generated On the other hand, comparing (71) with the general expression (34) we see that the contribution to the entropy production of the term represented by the photoelectrochemical affinity a_{ph} is dominant in this case.

IV. Conclusions

Table 1 summarizes the main differences among the three approaches for photoinduced reactivity at the sc−electrolyte interface, namely, the conventional (model A), the irreversible, stochastic (model B), and the irreversible, nonequilibrium thermodynamic approach (model C), presented here.

From a kinetic point of view no differences exist between models A and C, as both compute interfacial charge-transfer rate constant ratios from detailed balance and microscopic reversibility principles.Therefore, an expression for the photocurrent intensity like (7), which predicts a light intensity threshold for the photoinduced transfer of charge at the illuminated sc -electrolyte interface, is equally valid for models A and C. By contrast, model B rejects detailed balance and microscopic reversibility principles, which not only constitutes a serious drawback for describing equilibrium conditions in the dark but alsoobtains the rate constant ratios involved in interfacial, photoinduced charge-transfer kinetics. No formal description of the photocurrent intensity dependence on the photon fluxes is known for model B, although, according to their authors, it also predicts no light threshold for spontaneous, photoinduced interfacial transfer of charge.

From a thermodynamic point of view, both the equilibrium and the nonequilibrium model consider entropy loss as unavoidable, as long as photocurrent is flowing. However, only model C is able to introduce the entropy production as a new concept necessary for formalizing the entropy balance equation under

Figure 7. Energy balance scheme for the case of strong sc−electrolyte interaction, corresponding to an illuminated regenerative, n-type sc based photoelectrochemical cell under short circuit conditions. The high concentration of CB electrons at the sc surface, n_{so}, is scarcely modified by illumination (i.e., $n^* \approx n_{so}$), so that $E_{nF}^* = E_F - E_{redox}^o$. By contrast, $p^* \gg p_{so}$ for typical values of the hole transfer rate constant, k_p, if a reasonable photocurrent intensity is to be obtained (see (45)). Under this conditions, the contribution of CB electrons to the entropy production is negligible vs, the contribution of VB holes (i.e., $\sigma_n \ll \sigma_p$), so that $\nabla E_{nF}^* \ll \nabla E_{pF}^*$. This means that the entropy production is mainly controlled by the photoelectrochemical affinity, a_{ph}.

respectively, and X_n and X_p their respective conjugated forces. Therefore, under conditions of constant lattice temperature, according to (36)−(38), we can write:

$$\sigma_n = \frac{1}{T}\frac{J_{ph,st}}{q}(\nabla q\Phi - \nabla\mu_n) = \frac{1}{T}\frac{J_{ph,st}}{q}\nabla E_{nF}^* \quad (69)$$

and

$$\sigma_p = \frac{1}{T}\frac{J_{ph,st}}{q}(\nabla q\Phi - \nabla\mu_p) = \frac{1}{T}\frac{J_{ph,st}}{q}\nabla E_{pF}^* \quad (70)$$

Both σ_n and σ_p represent local values. A mean value of the generated entropy over the whole depletion layer (electric field region) of width W (see Figure 7) can be obtained by taking into account that

$$\langle\nabla E_{nF}^*\rangle = \frac{1}{W}\int_o^w \nabla E_{nF}^* \, dx = \frac{(E_{nF}^*)_s - (E_{nF}^*)_{x=w}}{W} = \frac{(E_{nF}^*)_s - E_{redox}^o}{W}$$

Similarly, $\langle\nabla E_{nF}^*\rangle = E_{redox}^o - (E_{nF}^*)_s/W = a_{ph}/W$. Therefore, we

TABLE 1: Comparison of the Different Models of Photoinduced Reactivity at the Semiconductor−Electrolyte Interface

	statistical mechanics principles	phenomenological relationship between refluxes and forces	no photocurrent light threshold	net photoelectrolysis light threshold	logarithmic free energy dependence on photon flux	entropy loss dependence on charge-transfer kinetics and photon flux	entropy production
equilibrium model (A)			X	X	X		
stochastic model (B)			X	X			
nonequilibrium model (C)	X	X	X	X	X	X	X

non equilibrium conditions. While model A only is able to predict that in an isolated system the entropy increases to a maximum defined by equilibrium conditions, model C predicts that under stationary conditions the entropy generated approaches a minimum. By contrast, the stochastic approach (B), although considering irreversibility, is not able to take into account the unavoidable entropy loss which must be present in any thermodynamic framework.

A formal description of the sc−electrolyte system under nonequilibrium illumination conditions is possible with the help of the quasi-Fermi level formalism, which allows important thermodynamic predictions, such as the existence of a light threshold for net photoelectrolysis and the logarithmic dependence of both the photogenerated free energy and the entropy loss on the photon flux (28), to be obtained. However, a full understanding of the physical meaning and thermodynamic implications of nonequilibrium concepts, like the entropy loss of a photoelectrochemical reaction, is only possible from the nonequilibrium model C. A main difference of model C with respect to model A concerns the capability of the former for predicting a formal relationship between the driving force of a photoelectrochemical reaction (photoelectrochemical affinity), the free energy stored (53) and the photocurrent intensity ((46) and (47)), as well as the existence of a logarithmic dependence of the photoelectrochemical activity on the photon flux (52). Finally, model C is also able to show how both kinetic parameters k_n and k_p involved in interfacial charge-transfer mechanisms can affect the maximum free energy stored by the photoelectrochemical system ((60)−(66), information not given by the equilibrium model which can be of interest for the design of efficient energy converter liquid junctions.

Appendix

Symbols

a = affinity
a_{cr} = critical affinity
a_{ph} = photoelectrochemical affinity
d = reaction layer thickness
d = diffusion coefficient
E_C = conduction band edge
E_{Cs} = conduction band edge at the surface
E_g = band gap
E_V = valence band edge
E_{Vs} = valence band edge at the sc surface ($x = 0$)
E_F = Fermi level
E_{pF}^* = quasi-Fermi level for valence band holes
$(E_{nF}^*)_s$ = quasi-Fermi level for conduction band electrons at the sc surface
$(E_{pF}^*)_s$ = quasi-Fermi level for valence band holes at the sc surface
$(E_{pF}^*)_{cr}$ = critical quasi-Fermi level for valence band holes at the sc surface
J^- = net cathodic current through the external circuit $(cm^{-2}s^{-1})$
$J_{ph,st}$ = stationary photocurrent (Acm^{-2})
j_c^- = rate of electron transfer from the conduction band to the electrolyte

j_c^+ = rate of electron transfer from the electrolyte to the conduction band
j_v^- = rate of electron transfer from the valence band to the electrolyte
j_v^+ = rate of electron transfer from the electrolyte to the valence band
j_i = diffusion flux
k_n = forward electron-transfer rate constant
k_p = forward hole transfer rate constant
k_n^{-1} = backward electron-transfer rate constant
k_p^{-1} = backward hole transfer rate constant
N_C = effective states local density at the bottom of the conduction band
N_V = effective states local density at the top of the valence band
$n_o(x)$ = local equilibrium concentration of conduction band electrons
n_{so} = surface equilibrium concentration of conduction band electrons
n_s' = surface concentration of conduction band electrons under applied bias
$n^*(x)$ = local excess population of conduction band electrons under illumination
n_s^* = surface excess population of conduction band electrons under illumination
$p_o(x)$ = local equilibrium concentration of valence band holes
p_{so} = surface equilibrium concentration of valence band holes
$p^*(x)$ = local excess population of valence band holes under illumination
p_s^* = surface excess population of valence band holes under illumination
$(p_s^*)_{cr}$ = critical surface excess population of valence band holes for net photoelectrolysis
p_s' = surface concentration of valence band holes under applied bias
S_v = entropy density
V_{cell} = potential bias
V_{oc} = open circuit voltage (photovoltage)
$(V_{oc})_{cr}$ = critical open circuit voltage for net photoelectrolysis
W = depletion layer width
ΔE_F = difference between conduction band edge in the bulk and Fermi level
ΔG = Gibbs energy of photogenerated electron−hole pairs
$(T\Delta S)_{mix}$ = total entropy of mixing
$(T\Delta S)_n$ = mixing entropy due to conduction band electrons
$(T\Delta S)_p$ = mixing entropy due to valence band holes
η_a = semiconductor anode intrinsic overpotential
η_c = metal cathode intrinsic overpotential
Φ = electric potential
Φ_o = illumination flux
$(\Phi_o)_{th}$ = threshold illumination flux for net photoelectrolysis
ϕ_s = bandbending
ϕ_{so} = bandbending under equilibrium conditions
λ = reorganization energy
μ = electron mobility
μ_i = chemical potential of species i
μ_n = chemical potential of CB electrons
μ_p = chemical potential of VB holes
ν_{ij} = stoichiometric coefficient
σ = entropy production
σ = entropy production due to CB electrons
σ_p = entropy production due to VB holes

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σ'_n = cross section for electron capture
σ'_p = cross section for hole capture

References and Notes

(1) Gerischer, H. *Semiconductor-Liquid Junction Solar Cells. Proceedings of the Conference on the Electrochemistry and Physics of Semiconductor-Liquid Interfaces Under Illumination*; Heller, A., Ed.; Electrochemical Society: Princeton, NJ, 1977; pp 1−19.

(2) Gerischer, H. *Topics in Applied Physics*; Seraphin, B. O., Ed.; Springer: Berlin, 1979; Vol. 31, pp 115−172.

(3) Gerischer, H. *J. Electroanal. Chem.* **1977**, *82*, 133.

(4) Williams, F.; Nozik, A. *Nature* **1978***, 271*, 137.

(5) Nozik, A. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189.

(6) Lewis, N. S. *Annu. Rew. Phys. Chem.* **1991**, *42*, 543.

(7) Kumar, A.; Santangelo, P. G.; Lewis, N. S. *J. Phys. Chem.* **1992**, *96*, 83.

(8) Shreve, G.; Lewis, N. S. *J. Electrochem. Soc.* **1995**, *142*, 112.

(9) Gregg, B. A.; Nozik, A. J. *J. Phys. Chem.* **1993**, *97*, 13441.

(10) Nozik, A. *J. Sol. Energy Mater.* Sol. Cells. **1995**, *38*, 73.

(11) Kopelman, R. *Science* **1988**, *241*, 1620.

(12) Grela, M. A.; Colussi, A. J. *J. Phys. Chem.* **1996**, *100*, 18214.

(13) Shockley, W. *Bell Syst. Tech. J.* **1949**, *28*, 435.

(14) Gerischer, H. *Adv. Electrochem. Eng.* **1966**, *4*, 249.

(15) Morrison, S. R. *Electrochemistry of Semiconductors and Oxidized Metal Electrodes;* Plenum Press: New York, 1980.

(16) Fahrenbruch, A. L.; Bube, R. H. *Fundamentals of Solar Cells*; Academic Press: New York, 1983.

(17) Archer, Mary D.; Bolton, James, R. *J. Phys. Chem.* **1990**, *94*, 8028.

(18) Onsager, L. *Phys. Rev.* **1931**, *38*, 2265.

(19) Nicolis, G.; Prigogine, I. *Self-Organization in Nonequilibrium Systems*; John Wiley & Sons: New York, 1977.

(20) Tauc, J. *Photo and Thermoelectric effects in Semiconductors*; Pergamon Press: Elmsford, NY, 1962

(21) Salvador, P. *New J. Chem.* **1988**, *12*, 35.

(22) Many, A.; Goldstein, Y.; Grover, N. B. *Semiconductor Surfaces*; North-Holland: Amsterdam, 1965.

(23) Morrison, S. R. *The Chemical Physics of Surfaces*; Plenum Press: New York, 1970.