

PHOTOCHEMICAL DETERMINANTS OF THE EFFICIENCY  
OF PHOTO GALVANIC CONVERSION OF SOLAR ENERGY

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ABSTRACT

A photogalvanic cell is a battery in which the cell solution absorbs light directly to generate species which, upon back reaction through an external circuit with the aid of suitable electrodes, produces electric power; photoactivation of the electrodes is not involved. The charge-carrying species have storage capacity if they are long-lived and can be prevented from engaging in degradative back reactions in bulk solution. The efficiency of a photogalvanic cell for the conversion of photon energy into electrical energy is determined by photochemical and electrochemical factors. Among the latter are the choice of electrode materials and the kinetics of electron transfer at the heterogeneous surfaces. In this paper we examine the photochemical determinants of the efficiency of photogalvanic cell operation: the absorption spectral characteristics of the cell solution, the efficiency of formation of separated charge carriers, and the lifetimes of the carriers toward back electron transfer. Modulation of bulk solution dynamics can be achieved by variation of the solution medium. The photochemical determinants are discussed with particular reference to the use of thionine or  $\text{Ru}(\text{bpy})_3^{2+}$  as the light absorbing species.

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## INTRODUCTION

It is obvious that the practical value of a device that can effect the direct conversion of solar energy into electricity with the capacity for storage would be enormous. Such a rechargeable solar battery could have applicability as a mobile source and in areas isolated from an electric grid system. In principle, photogalvanic devices can achieve these goals. A photogalvanic cell is a battery in which the cell solution absorbs light directly to generate species which, upon back reaction through an external circuit with the aid of suitable electrodes, produces electric power; photoactivation of the electrodes is not involved. In its simplest terms, photoexcitation of the absorbing species leads to an excited state which can undergo reductive or oxidative quenching to form charge carriers. The conversion of charge carriers to the original substrates at suitable electrodes provides electrons that can be driven through an external circuit to perform useful work. The capacity for storage derives from the lifetimes of the charge carriers; the longer lived the charge carriers with respect to energy degradative back electron transfer in bulk solution, the greater the opportunity for storage to pass from the microtime domain into the macrotime. Efficient storage would be achieved if the charge carriers were kinetically stable.

In this paper, the photogalvanic process is examined in terms of the photochemical determinants which establish the efficiency of such a cell with particular reference to the use of thionine and  $\text{Ru}(\text{bpy})_3^{2+}$  as the light absorbing species in solution. As will be seen, the current state of the art does not permit the utilization of photogalvanic cells as practical solar energy devices at the present time but some research approaches for future development are presented.

## THE PHOTOGALVANIC PROCESS

A photogalvanic cell as defined in the Introduction is a closed-cycle quantum device which operates without the net consumption of any chemical component (except through undesirable side reactions or other losses). In a photogalvanic transducer, absorbed quanta drive a redox reaction which, in the ground state, is endergic; the

prompt, spontaneous reversal of this reaction through the external electrical circuit restores the system to its original composition. In a photogalvanic storage cell, spontaneous reversal does not take place promptly. Products of the photoredox reaction are stored by some means for an essentially infinite period but ultimately are caused to react through the external circuit to restore the original composition. In a photocatalyzed galvanic cell, production of electricity is associated with a net change in the chemical composition of the system. As a result, the cell cannot be operated in multiple closed cycles.

There are five fundamental steps inherent in photochemical conversion (1): 1) absorption of light; 2) generation of charge carriers; 3) transport of charge carriers to electrodes; 4) electron exchange between charge carriers and electrodes; 5) delivery of current to load. Step 1 is simple in concept and involves matching the absorption spectrum of the cell solution as well as possible to the insolation spectrum by means of the design of absorbing species and sensitizers. Step 2 may involve one or more elementary reactions and must produce charge carriers which can store the energy derived from the solar photons long enough to allow the following step to occur. Step 3 requires the transport of the charge carriers to the electrodes to compete with their bulk back reactions in homogeneous solution; by means of device design and chemical tuning, the solution lifetime of charge carriers can be maximized. Options available in step 4 include diffusion-controlled electron transfer at reversible electrodes and efficient blocking of the charge carriers at selective electrodes. Manipulation of these options is essential to the ultimate achievement of practical photogalvanic devices. When the electrodes are conductors, step 5 is trivial. When a semiconductor is used as an electrode to achieve selectivity, resistive losses in the electrode can be substantial if suitable precautions are not taken.

#### Photogalvanic Devices and Electrical Output

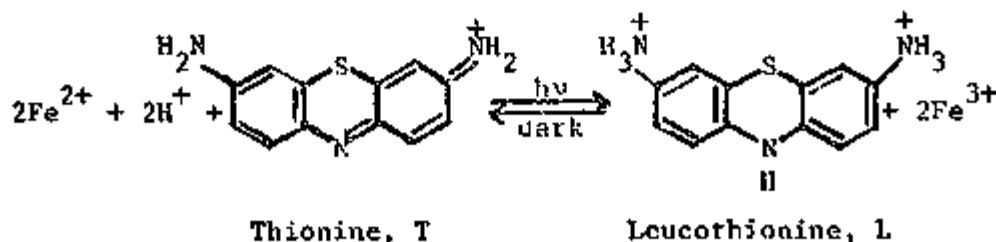
A number of analyses of the general thermodynamic and kinetic aspects of the electrical output of photogalvanic cells have been published (2-4). It is inconvenient to separate such analyses completely from device specifics so that in this section we shall discuss the electrical

output of three types of photogalvanic converters utilizing the iron-thionine system: "primitive beaker" cell, the totally illuminated thin-layer (TI-TL) transducer, and storage cells.

After the discovery over forty years ago (5,6) that thionine is reversibly photoreduced by  $Fe^{2+}$  in acidic aqueous solution, Rabinowitch (7) explored the possibility of utilizing the system in the construction of a photogalvanic cell for solar energy conversion. In the "primitive beaker" cell shown in Figure 1, the electrodes are identical with one illuminated and the other in the dark. The open circuit voltage,  $V_{oc}$ , is ideally the difference in the reversible potentials at the two electrodes. For the iron-thionine system, the concentration of leucothionine is negligible at the dark electrode so that the exchange current is determined entirely by the iron couple. The potential at the dark electrode is given by the Nernst expression in equation 1 (8) where  $E_{Fe}^{\circ}$  is the standard

$$E_{\text{dark}} = E_{Fe}^{\circ} + 0.06 \log\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right)_{\text{dark}} \quad (1)$$

reduction potential of the  $Fe^{3+}/Fe^{2+}$  couple and the terms in the square brackets represent the activities of the species. The potential at the illuminated electrode is a complex function and depends on the concentrations of all the redox species at the electrode (8). The expression for this potential can be simplified for an ideal electrode by assuming that the electron transfer rate constants for all the redox species are the same and further simplified by assuming that the photostationary concentration of the half-reduced dye, semithionine, is negligible. The result is equation 2 where  $f = F/RT$ ,  $F$  is the Faraday in coulombs,  $E_{\text{light}}$  is the potential of the illuminated electrode,  $E_{Fe}^{\circ}$



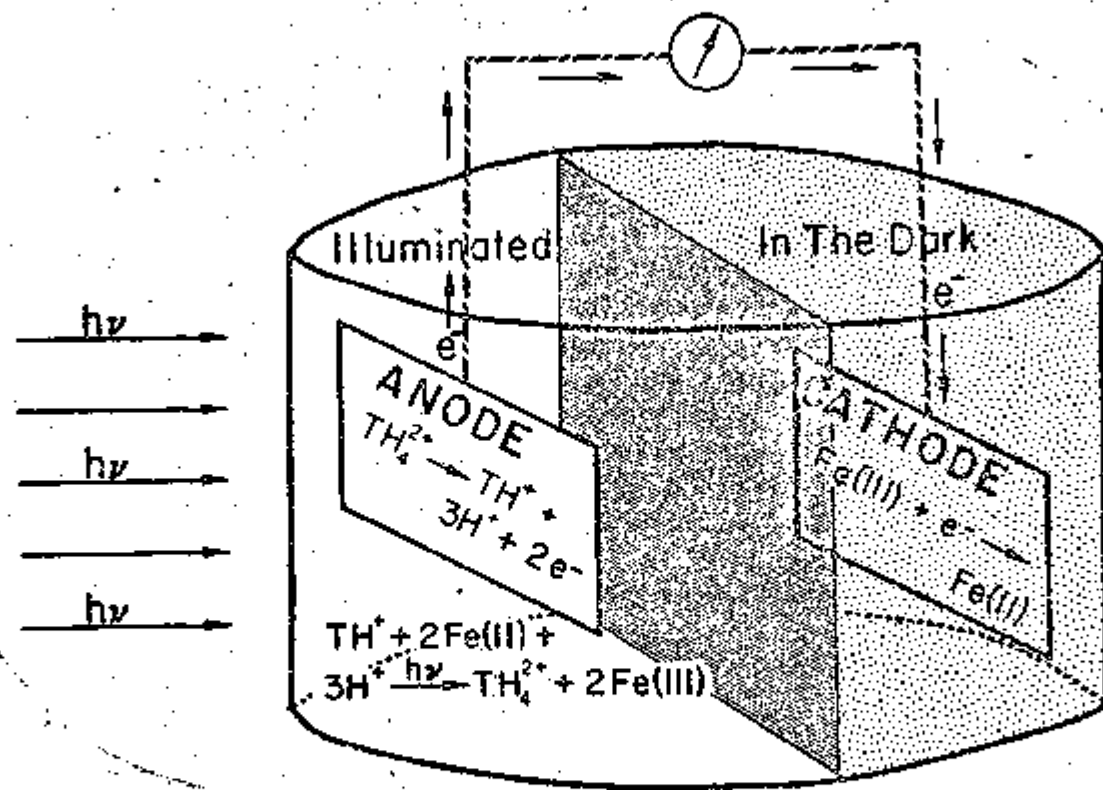
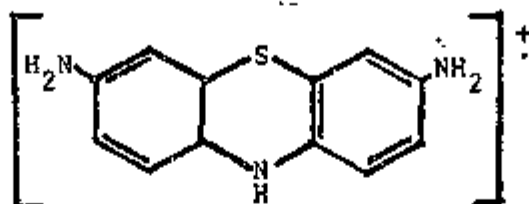


Figure 1. "Primitive-beaker" iron-thionine photogalvanic cell. TH<sup>+</sup> = thionine, TH<sub>4</sub><sup>2+</sup> = leucothionine, both at pH 2. The overall light-driven cell reaction and the spontaneous energy-producing reactions at the electrodes are shown.



Semithionine, S

is the standard reduction potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple,  $E_{T \rightarrow S}^0$  is the standard potential for the one-electron reduction of thionine, and  $E_{S \rightarrow L}^0$  is the standard potential for the one-electron reduction of semithionine. The terms in the square brackets represent the activities

$$\exp(fE_{\text{light}}) = \frac{[\text{Fe}^{3+}] \exp(fE_{\text{Fe}}^0/2) + 2[\text{T}] \exp(fE_{T \rightarrow S}^0/2)}{[\text{Fe}^{2+}] \exp(-fE_{\text{Fe}}^0/2) + 2[\text{L}] \exp(-fE_{S \rightarrow L}^0/2)} \quad (2)$$

of the various species in the photostationary state. Analogous terms would be appropriate for other photoredox systems. The potential of the "primitive beaker" photogalvanic cell under open circuit photostationary conditions is equal to  $E_{\text{dark}} - E_{\text{light}}$  as calculated from equations 1 and 2.

The current produced by a "primitive beaker" photogalvanic cell with ideally reversible electrodes depends on the composition of the bulk solution in the photostationary state under short-circuit or other conditions of current withdrawal and on the rate of diffusion of charge carriers to the electrodes. This current is related to various system parameters via Nernst's diffusion current relationship (9), equation 3, where  $n$  is the number of redox equivalents per mole of a given charge carrier,  $F$  is the Faraday,  $A$  is the electrode area,  $D$  is the diffusion coefficient of a given charge carrier,  $C_b$  is the concentra-

$$i = n F A D C_b / \delta \quad (3)$$

tion of a given charge carrier in bulk solution under photostationary conditions, and  $\delta$  is the thickness of the diffusion layer. The situation is complicated when electrodes are reversible to both redox couples (2) since the current cannot be related to the bulk concentration of a single charge carrier at each electrode. A detailed treatment of this is beyond the scope of this presentation. For "primitive beaker" cells, only very low sunlight engineering efficiencies (S.E.E.  $\leq 10^{-3}\%$ ) have been



reported. The crucial figure of merit in evaluating the efficiency of solar energy conversion is S.E.E. as defined in equation 4 for conversion to electrical power or energy.

$$\text{S.E.E.} = \frac{\text{electrical power or energy delivered to load}}{\text{incident sunlight power or energy}} \times 100$$

(4)

The totally illuminated thin-layer (TI-TL) photogalvanic cell was first described by Clark and Eckert (10) and a number of studies of the behavior of the iron-thionine photoredox system in such cells have been reported (8,11-17). In TI-TL cells, at least one electrode is selective; ideally, a selective electrode completely blocks one redox couple while it is completely reversible to the other. Greatest efficiency would be achieved with a TI-TL cell in which each electrode was perfectly selective for a different couple. Figure 2 shows a schematic drawing of a TI-TL iron-thionine cell in which the anode is *n*-type SnO<sub>2</sub> which responds selectively to the thionine/reduced thionine couple while non-selective materials (such as Pt, indium tin oxide, or Cd<sub>2</sub>SnO<sub>4</sub>) are used as cathodes. TI-TL cells offer the possibility of development as practical area devices analogous to solid-state photovoltaic devices. The best S.E.E. value reported (12) for a TI-TL iron-thionine cell, ~0.06%, is more than 100 times less than S.E.E. values readily achieved with both solid-state and liquid-junction (18) photovoltaic devices. The theoretical upper limit of S.E.E. of TI-TL iron-thionine photogalvanic cells is 2-3% and with sensitization to the blue is 5-10%.

Little research on photogalvanic storage cells has been reported. Such devices require long-term storage of potential energy in a galvanic cell which can be charged directly by light and recharged by light after each cycle during which its potential energy is withdrawn as electricity. The ideal system for such storage would be one in which the photoredox reaction produced endergic products which would release their free energy efficiently upon back reaction at the electrodes but at a negligible rate by back reaction in bulk medium. The back reaction through electron transfer at suitable electrodes would take place only when the external electrical circuit was closed between the electrodes. No such system appears to

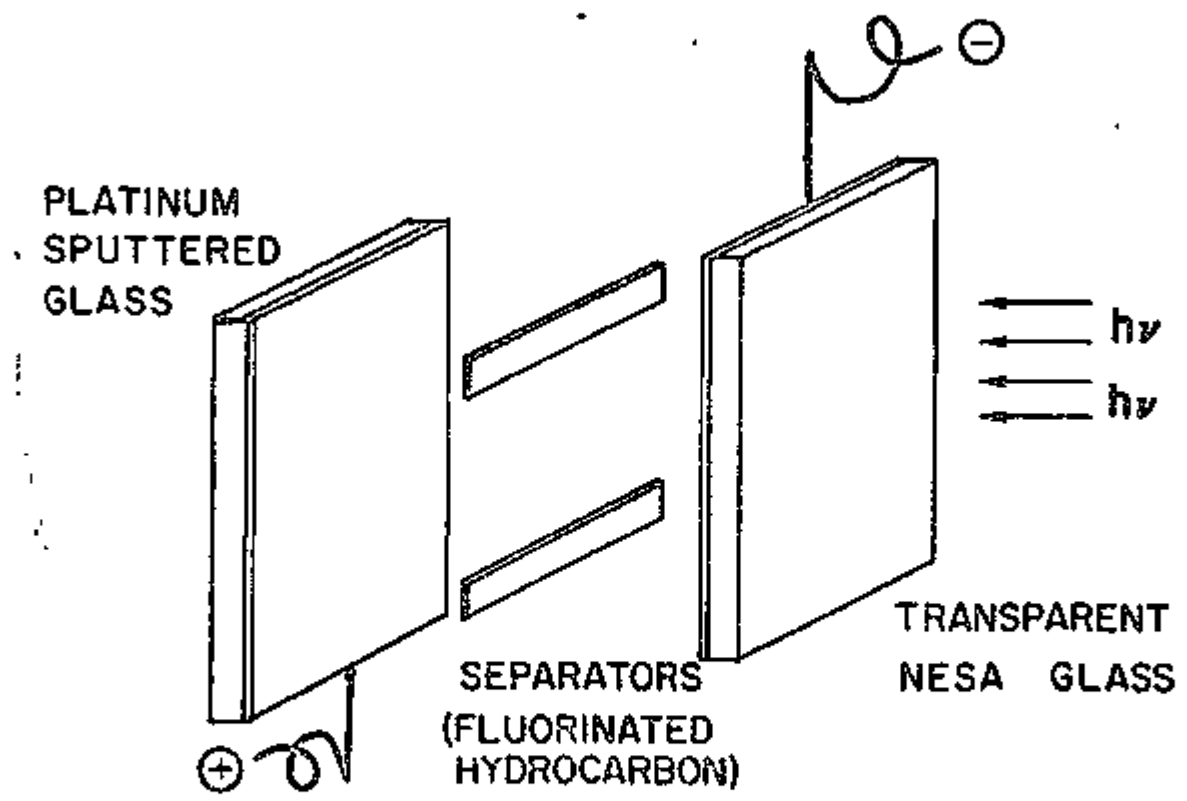


Figure 2. Totally illuminated thin-layer (TI-TL) photo-galvanic cell. NESA glass has a surface layer of transparent n-type SnO<sub>2</sub>. Separation between electrodes is typically 25-80  $\mu\text{m}$ .

have been reported. The design of such systems is an important and exciting challenge to photochemists.

At least two approaches to photogalvanic storage have been developed which do not depend upon the inertness of photoredox products in bulk medium. Both approaches involve physical separation, one of reactants, the other of products. The process of charging a photogalvanic storage cell with reactants separated requires that light-driven electron transfer takes place through an external circuit or an asymmetric bilayer membrane. Storage via physical separation of photoredox products requires separation techniques, e.g., phase separation, which are fast compared to spontaneous back reaction in bulk medium. The photoreduction of thionine to leucothionine by  $\text{Fe}^{2+}$  in the presence of excess acetate ion, which is irreversible because of the precipitation of insoluble ferric acetate (19), could conceivably be the basis for a "products separated" photogalvanic storage cell; it does not appear to have been exploited for this purpose. The relatively slow rate of the bulk back reaction of leucothionine with the EDTA complex of Co(III) has been exploited in the extraction of leucothionine into ether from aqueous medium; the back reaction of the separated products via an external circuit has been demonstrated (20).

#### THE ELECTROCHEMICAL DETERMINANTS

Regardless of the type of photogalvanic cell, efficient electron transfer must occur between photochemically-generated separated charge carriers and appropriate electrodes. The determinants of the electrode processes in "primitive beaker" cells, in which electrodes are reversible to all the redox couples, have been discussed in the previous section. If practical photogalvanic cells are ever achieved, it appears likely that electrodes selective to particular redox couples will be employed. Selectivity is not, however, the only requirement. In addition, the electrode must not catalyze back reaction of charge carriers on its surface. Such back reaction is equivalent to shorting a circuit in parallel with load. Surface catalysis of the oxidation of leucothionine by  $\text{Fe}^{3+}$  on its *n*-type  $\text{SnO}_2$  selective anode has been identified as a major loss factor in TI-TL iron-thionine cells (16).

### Requirements for Electrode Selectivity

The theory of the phenomena at the interface between semiconductors and electrolytic solutions has been developed by Gerischer (21) and by Levich (22). This theory has been applied extensively to photoelectrochemical (liquid-junction) devices (23) in which quanta are absorbed by the semiconductor electrodes. Application to photogalvanic devices is simpler because excitation of the semiconductor is not involved and key features of this application follow.

- 1) The efficiency of electron transfer across the interface between electrolyte and semiconductor is largely governed by relationships between the redox potentials of electrolyte couples and the energies of bands of the semiconductor. Reduction potentials on the NHE scale in aqueous solution can be converted to the energy scale used for semiconductor levels which takes the energy of a free electron in vacuum as zero, by reversing the sign of the reduction potential and subtracting 4.6.
- 2) Electron transfer between a redox couple and a semiconductor electrode is blocked, in whole or in part, if the redox potential of the couple falls within the gap between the highest energy level of the valence band of the semiconductor and the lowest energy level of its conduction band. In general, blocking is more complete the farther the redox potential of the couple is from the two band edges. The relationship between redox potential and semiconductor energy levels depends on the magnitude of the band gap, the energy of the valence (or conduction band edge), and the redox potential of the couple under these conditions of use. It should be noted that since the band gap determines the wavelength of light above which a semiconductor does not absorb light, band gaps of 3.5V or greater (354 nm or less) are particularly appropriate for photogalvanic solar devices because essentially 100% of the insolation spectrum at sea level is at wavelengths longer than this value.
- 3) n-Type semiconductors are best suited for use as selective anodes while p-type semiconductors are most appropriate as selective cathodes. The electron energy levels of an n-type semiconductor bends upwards near the interface with an electrolytic solution (see Figure 3) while band-bending is downward for a p-type semiconductor. Thus, electrons can flow into the conduction band of an n-type semiconductor from a redox couple with a potential

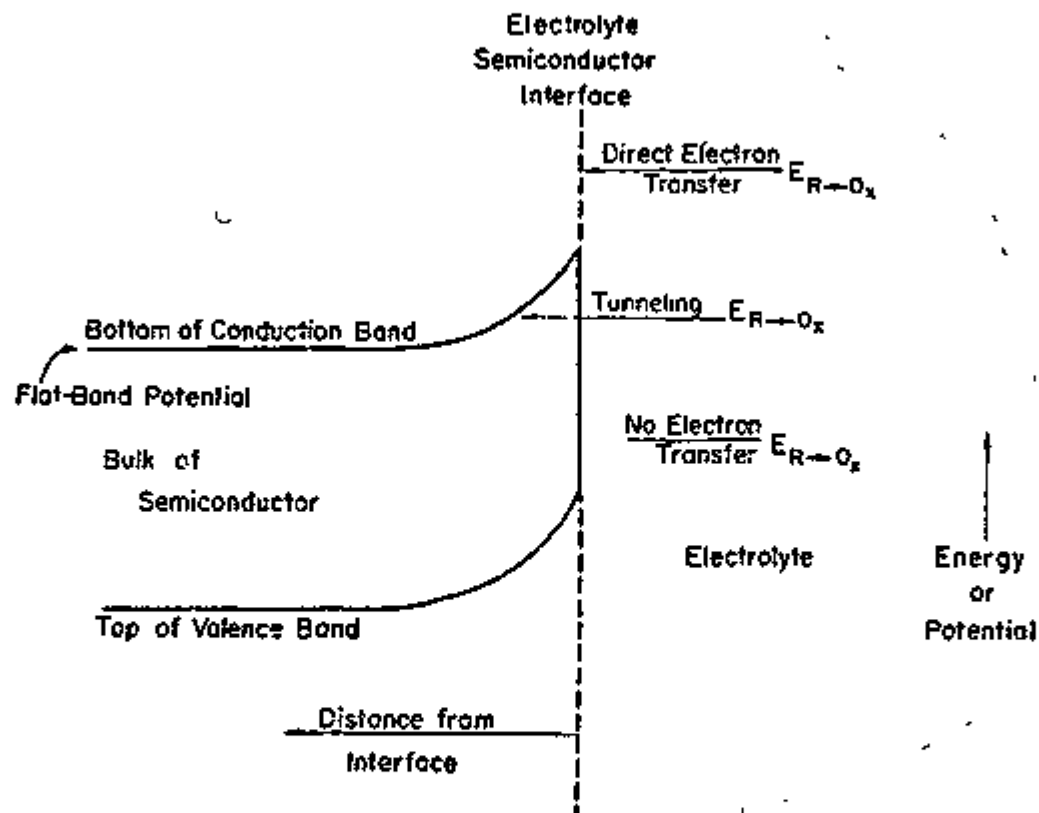


Figure 3. Diagram of energy relationships in the vicinity of the interface between an n-type semiconductor and redox electrolyte solutions.

at or above the bottom edge of the conduction band at the interface. If the redox potential is below that level but at least as high as the flat-band potential of the n-type semiconductor (i.e., the lower edge of the conduction band in the bulk of the semiconductor and outside the band-bending region), electron transfer to the electrode may still occur by tunneling as illustrated in Figure 3. Similarly, electrons can flow from the conduction band of a p-type semiconductor to a redox couple, the potential of which lies below the bottom edge of the conduction band at the interface or at least below the flat-band potential. Many n-type semiconductors are known which have large enough band gaps to be transparent to sunlight (>3.5V) but few, if any, transparent p-type semiconductors are available.

#### Iron-Thionine TI-TL Cell with Selective SnO<sub>2</sub> Anode and Poorly Selective Cathode

It has been shown that conversion of visible light to electricity by the iron-thionine TI-TL photogalvanic transducer with n-type SnO<sub>2</sub> anode and Pt, indium tin oxide, or Cd<sub>2</sub>SnO<sub>4</sub> cathode is largely due to the preference of the anode for accepting electrons from leucothionine rather than from Fe<sup>2+</sup> (14-16). Selectivity is limited with the result that photogalvanic voltages are substantially reduced because the anode potential reflects a mixed exchange current. Exchange with the dye couple predominates but exchange with the iron couple is significant (8). The cathodic voltage reflects a mixed potential in which exchange by the iron couple predominates.

It has been shown that essentially all charge carriers generated in the TI-TL iron-thionine photogalvanic cell reach the electrodes which are separated by 25 or 80 μm. Incompleteness of selectivity of electrode processes does not fully account for deficiency of output compared to that calculated from the photostationary compositions. A loss factor of 4-8 appears to be due to inefficient transfer of electrons between charge carriers and electrodes. This inefficiency has been ascribed to complexation of Fe<sup>3+</sup> by leucothionine (24) adsorbed on SnO<sub>2</sub> followed by back reaction of a portion of the adsorbed complexes, desorption of the other complexes, and diffusion back into the bulk solution (16).

## THE PHOTOCHEMICAL DETERMINANTS

Even if electron transfer at the electrodes were perfectly efficient and the maximum current and voltage from the photogenerated charge carriers could be achieved, the efficiency of photogalvanic conversion of solar energy would be limited by those factors that are part of the photochemical mechanism: the absorption spectral characteristics of the cell solution, the efficiency of formation of the separated charge carriers, and the lifetimes of the carriers toward back electron transfer. In this section of the paper we shall discuss the general nature of the photochemical determinants, their limitations with regard to thionine and  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine) as the absorbing species, and some means which are available for varying and optimizing these parameters. The use of thionine in photogalvanic cells has been discussed in previous sections;  $\text{Ru}(\text{bpy})_3^{2+}$  has also been shown (25) to engage in photogalvanic action.

### Absorption of Light

The essential requisite for any photochemical process is the absorption of light; the ideal solar energy absorber is one which could absorb all the photons from the sun that impinge upon it with the concomitant generation of the reactive excited states that lead to the separated charge carriers. In reality, not all the photons will be absorbed nor will they all, even if absorbed, lead to the reactive excited states and charge carriers. The absorption of light is a wavelength-dependent phenomenon governed by the Beer-Lambert law,  $A_\lambda = \epsilon_\lambda l c$ , where  $A_\lambda$  is the absorbance of the solution at a particular wavelength,  $\epsilon_\lambda$  is the molar absorptivity ( $\text{M}^{-1}\text{cm}^{-1}$ ) of the solution at that wavelength,  $l$  is the pathlength (cm) of the absorbing solution, and  $c$  is the concentration (moles liter $^{-1}$ ) of the absorbing species. If the absorbance of the solution were unity at all wavelengths, 90% of the sunlight would be absorbed; if  $A = 2$ , 99% of the sunlight would be absorbed. In order to achieve that high absorption of all the wavelengths of sunlight, the pathlength and/or concentration of the absorbing solution would have to be large enough to offset the low values of  $c$  at some wavelengths. Since  $c$  is not uniform across the wavelength range, the very high absor-

bancies that must occur at some wavelengths can be limiting factors; absorption of light would be virtually complete in a very small depth (perhaps less than 1mm) at the window. The resultant inhomogeneity of excited state and charge carrier concentration across the bulk of the solution would create kinetic and diffusional limitations. Long pathlengths present the potential problem of the diffusion of charge carriers through a large bulk of solution. From the practical standpoint, large cell pathlengths will increase the volume and weight of solution that must be contained and high concentrations of absorbers can be equated with a high cost of expensive materials.

Assuming that a pathlength of  $\sim 10$  cm and an absorber concentration of  $\sim 10^{-3}M$  probably represent upper limits, an absorbance of unity is achieved for  $\epsilon_{\lambda} \geq 10^2 M^{-1}cm^{-1}$ . In practice,  $\epsilon_{\lambda}$  values of  $< 10^3 M^{-1}cm^{-1}$  are probably not very useful for reasonable pathlengths. This is not to say that weakly absorbing materials, due to low values of  $\epsilon$  or  $c$  cannot be used; cells could be stacked so as to achieve a long effective pathlength. Such an approach, however, may pose severe engineering problems.

Values of  $\epsilon_{\lambda} > 10^3 M^{-1}cm^{-1}$  are characteristic of highly allowed electronic transitions (charge transfer,  $\pi-\pi^*$ ) which will have threshold energies corresponding to the O-O transition. While there may be forbidden (d-d, S-T) transitions at energies lower than the highly allowed transition, their forbiddenness causes  $\epsilon_{\lambda}$  to be low and renders them of limited practical utility. Clearly, the most effective materials for use as solar harvesters will be those that absorb strongly in the visible and near-uv regions of the spectrum. Figure 4 shows the absorption spectra of thionine and  $Ru(bpy)_3^{2+}$  in aqueous solution. It is easy to see why these materials have been popular solar absorbers; yet, even under the most favorable conditions of pathlength and concentration, only a small fraction of the solar radiation at air mass 1 (Figure 5) could be absorbed. Even if all the other characteristics of photogalvanic cells employing these materials were perfectly efficient, such cells would be limited by the fraction of the solar output absorbed by the solution.

It being a shame to waste all those potentially perfectly good solar photons, approaches must be taken to improve the absorption characteristics of the medium, especially to the red; there is no lack of chromophores



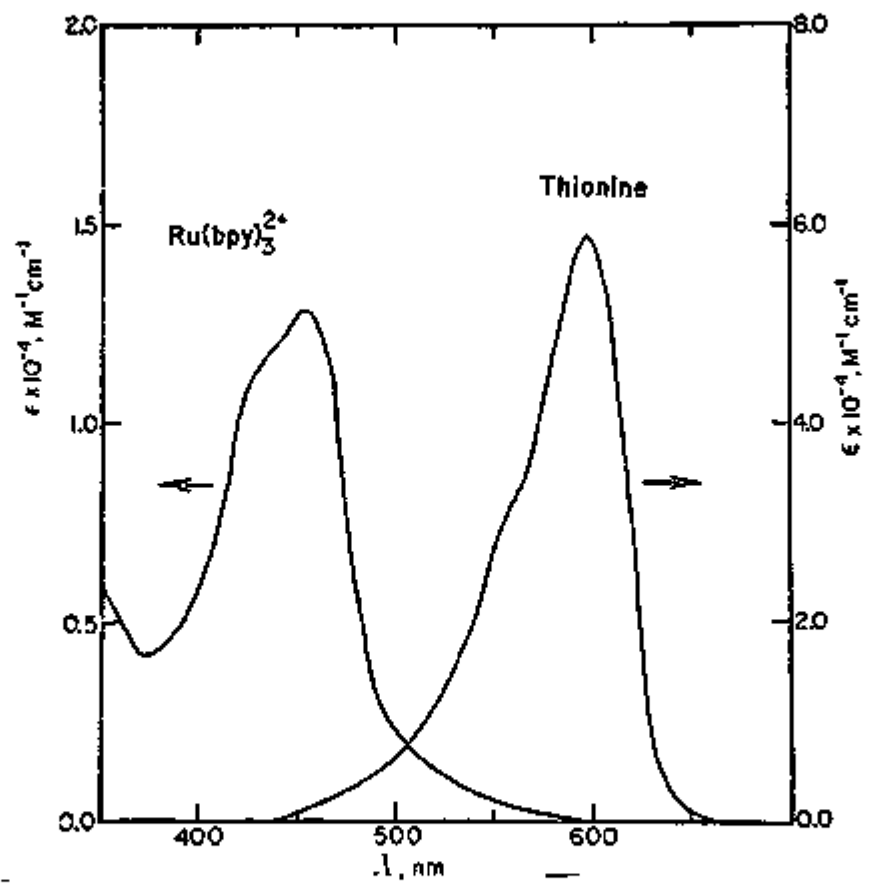


Figure 4. Absorption spectra of thionine (pH 2) and Ru(bpy)<sub>3</sub><sup>2+</sup> in aqueous solution.

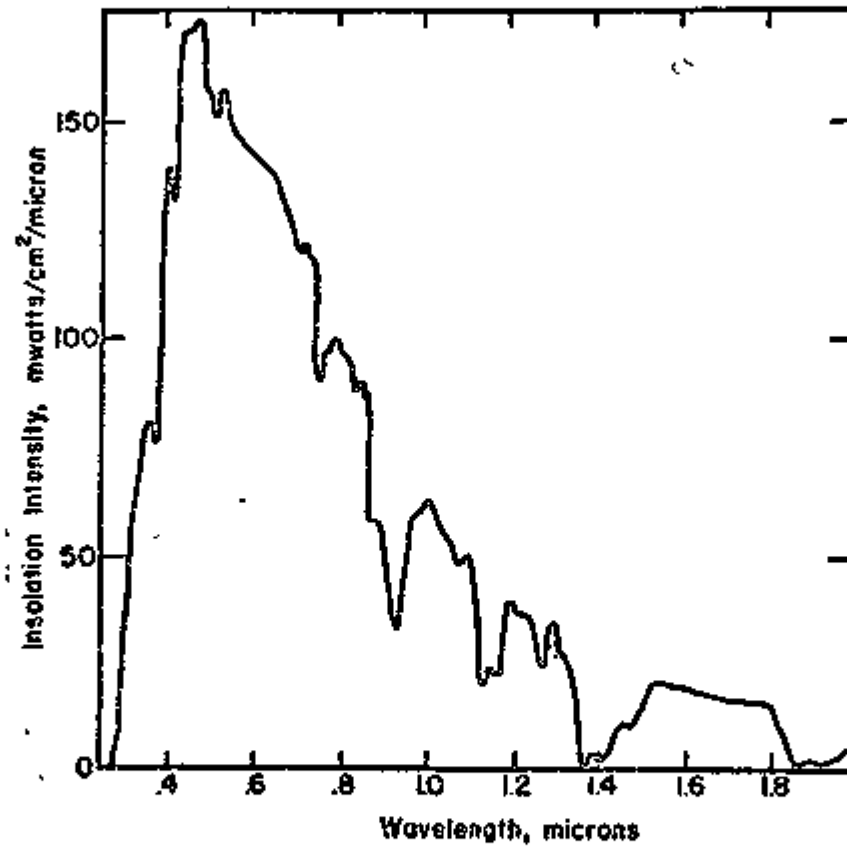


Figure 5. Insolation spectrum at air mass 1 (sea level with sun at the zenith).

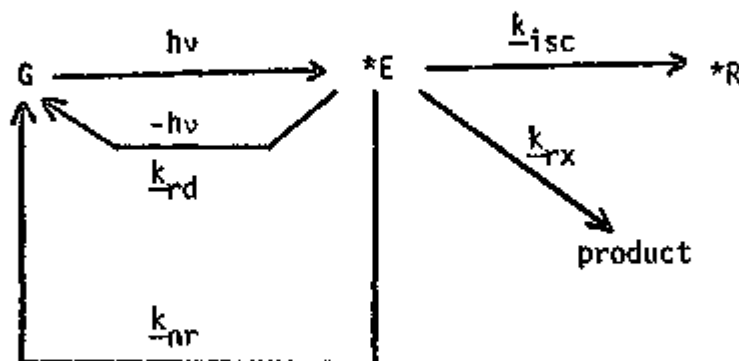
for the uv region. Molecular modification of thionine to methylene blue results in a substantial shift of  $\lambda_{\max}$  to 665 nm ( $\epsilon_{\max}$   $8.0 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$ ). For  $\text{Ru}(\text{bpy})_3^{2+}$ , substitution of phen (=1,10-phenanthroline) for bpy or substitution on the polypyridyl rings has little effect on  $\lambda_{\max}$  or the shape of the visible absorption envelope (26,27). Some red shift of  $\lambda_{\max}$  to 473 and 501 nm is observed for  $\text{Ru}(\text{terpy})_2^{2+}$  and  $\text{Ru}(\text{TPTZ})_2^{2+}$  (terpy = 2,2',2''-terpyridine; TPTZ = 2,4,6-tri(2-pyridyl-s-triazine)) (26). These effects are very modest but they show that alternation of the ligand structure is a reasonable approach. Recently, Dose and Wilson (28) prepared mono- and binuclear Ru(II) complexes containing N-bound aromatic ligands which show  $\lambda_{\max}$  close to 600 nm. Whether these or other complexes yet to be synthesized will possess the other qualities necessary for photogalvanic conversion remains to be seen.

In most cases, the intense visible absorption bands and those further to the blue are separated by regions of significantly lower absorbance. In order to utilize those solar photons, sensitizers can be employed to absorb light and transfer energy from the excited state of the sensitizer to the photochemically active species. The requirement is for the energy of the excited state of the donor to be higher than the energy required to reach the populated excited state of the acceptor. As a result, sensitization to the blue of the intense absorption band of the acceptor can be achieved as has been demonstrated for mixtures of dyes with thionine and methylene blue (29). Sensitization to the red of the intense singlet absorption band is limited by the energetics of the lowest, and presumably reactive, excited state.

#### Formation of Separated Charge Carriers

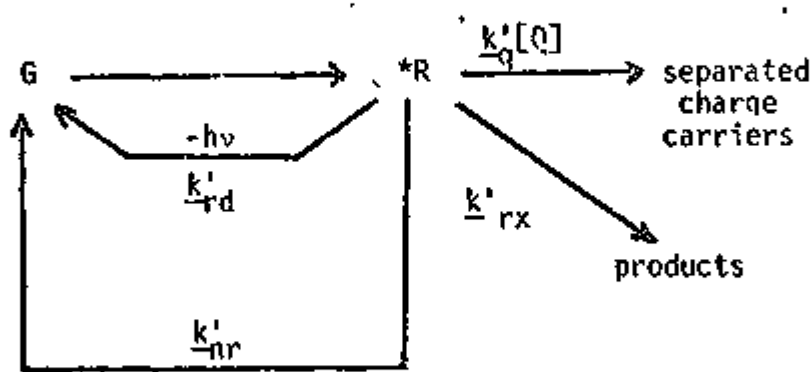
There are many physical and chemical steps between the formation of the initial excited state as a result of the light-absorption process and the separated charge carriers. In the first place, the initial excited state may not be the reactive state that is the precursor of the charge carriers. If the absorber is an organic molecule, excitation in the intense absorption band produces the lowest excited singlet state, the lifetime of which is of the order of  $10^{-9}$ s. A lifetime that short

precludes efficient quenching; even if the quenching rate constant were in the diffusion-controlled region ( $\sim 10^{10} \text{M}^{-1} \text{s}^{-1}$ ), a quencher concentration of  $\sim 1 \text{M}$  would be required in order to intercept 90% of the excited state. Intersystem crossing from the lowest singlet excited state to the lowest triplet excited state, which, being longer lived than the singlet is more likely to be the reactive excited state that leads to the charge carriers, competes with radiative and non-radiative internal conversion back to the ground state and degradative reactive modes. Using the symbols G, \*E, and \*R for the ground, initially excited, and reactive excited states, respectively, the scheme can be generalized with  $k_{rd}$ ,  $k_{nr}$ ,  $k_{rx}$ , and  $k_{isc}$  representing the rate constants for radiative, non-radiative, reactive, and intersystem crossing decay of \*E, respectively. Inasmuch as the quantum yield of formation of the excited state populated in the absorption process must be unity, the quantum yield of formation of \*R is dictated by the efficiency of the intersystem crossing step ( $\eta_{isc}$ ) in competition with the energy degradation modes:  $\eta_{isc} = k_{isc} / (k_{rd} + k_{nr} + k_{rx} + k_{isc})$ . For thionine as for aromatic molecules in general, the major mode of decay of the lowest excited singlet state is intersystem crossing to the triplet state so that  $\eta_{isc} = \phi_{*R} + 1$ . For  $\text{Ru}(\text{bpy})_3^{2+}$ , where \*R corresponds to a metal-to-ligand charge transfer excited state involving promotion of a metal-centered  $d$  electron into highly delocalized  $\pi^*$  ligand orbitals, population of \*R occurs with nearly unitary efficiency (30). In these systems, the quantum yield of formation of \*R cannot be viewed as a severe limitation to the efficiency of photogalvanic conversion



as long as the degradation of \*E to some inactive product does not occur to any meaningful extent. Such degradation would preclude the use of the system in the required cyclic manner. However, if an interesting photogalvanic system were developed in which  $\eta_{isc}$  were not nearly unity, the internal or external heavy-atom effect could be used to enhance intersystem crossing.

With the quantum yield of formation of the reactive excited state,  $\phi_{*R}$ , approximately unity, attention must be focused on the redox reactions that quench \*R and generate the separated charge carriers. In the absence of redox quencher, the decay of \*R is via radiative, non-radiative, and reactive modes with  $k'_{rd}$ ,  $k'_{nr}$ , and  $k'_{rx}$  representing the rate constants of those processes. The intrinsic lifetime of \*R is dictated by those values of  $k'$ :  $\tau_{*R}^0 = 1/(k'_{rd} + k'_{nr} + k'_{rx})$ ; it is assumed that \*R is the lowest electronically excited state of the absorber so that transitions to other excited states can be ruled out. In the presence of the quencher at a concentration [Q], the quenching reaction, with a second-order rate constant of  $k'_q$ , competes with the intrinsic modes so that the lifetime of \*R is reduced:  $\tau_{*R} = 1/(k'_{rd} + k'_{nr} + k'_{rx} + k'_q[Q])$ . The efficiency of the quenching reaction,  $\eta_q$ , is given simply as  $\tau_{*R}^0 k'_q [Q] / (\tau_{*R}^0 k'_q [Q] + 1)$ . It is easy to see that  $\eta_q \rightarrow 1$  as [Q] increases so that  $\tau_{*R}^0 k'_q [Q] \gg 1$ . Thus, if  $\tau_{*R}^0$  is small, a high concentration of Q and a large value of  $k'_q$  must be combined in order for the quenching reaction to compete. For example, in order to quench ~90% of \*R,  $\tau_{*R}^0 k'_q [Q] \sim 10$ ; if  $\tau_{*R}^0 \sim 10^{-6}$  s and  $k'_q$  were in the diffusion-controlled region ( $\sim 10^{10} M^{-1} s^{-1}$ ), [Q] has to be of the



order of  $10^{-3}M$ . In order to quench ~99% of  $*R$ ,  $[Q]$  would have to be  $\sim 10^{-2}M$ ; if  $k'_q$  were less than  $\sim 10^{10}M^{-1}s^{-1}$ , proportionally higher concentrations of  $Q$  would have to be used.

It is clear that the parameters available to control  $n_q$  are  $\tau_{*R}^0$  and the product  $k'_q[Q]$ . It is advantageous to have  $\tau_{*R}^0$  and  $k'_q$  as large as possible so as to be able to quench  $*R$  without requiring the concentration of  $Q$  to be so large as to exceed its solubility limit, interfere with the light absorption process, or interfere with the electrochemical aspects of the cell.

The value of  $\tau_{*R}^0$  for a particular excited state is fixed by nature although molecular environment can have an effect due to changes in the rate constants of non-radiative and reactive modes; radiative decay, where it exists at all in fluid media, is generally a small fraction of the total decay paths and is relatively insensitive to molecular environment. For thionine, the intrinsic lifetime of the lowest triplet state is 7-8  $\mu s$  (31). For  $Ru(bpy)_3^{2+}$ , the lifetime of the charge transfer excited state is little affected by changes in the solution medium;  $\tau^0$  ranges from 0.60  $\mu s$  in aqueous solution (32) to 1.0  $\mu s$  in  $D_2O$  (33) and is 0.76  $\mu s$  in  $CH_3OH$  (32). Variation of the substituent nature of the polypyridyl ligands does result in modest changes in  $\tau^0$  with 0.92  $\mu s$  for  $Ru(phen)_3^{2+}$ , 1.8  $\mu s$  for  $Ru(5,6-(CH_3)_2phen)_3^{2+}$  (34), and  $\sim 2 \mu s$  for  $Ru(II)$  complexes containing hydrophobic ligands (27). Unfortunately, the more promising complexes from the point of view of their absorption characteristics,  $Ru(terpy)_2^{2+}$  and  $Ru(IPTZ)_2^{2+}$ , have very short intrinsic excited state lifetimes of  $< 5 ns$  (26,35) which effectively rule out their applicability as efficient generators of separated charge carriers.

Any degradative reactions of  $*R$  that do not lead to separated charge carriers and are competitive with the desired redox quenching reaction are wasteful. These include energy transfer quenching and interaction with the solvent and other solutes. For excited triplet states of aromatic molecules and the excited states of metal complexes, rapid energy transfer quenching by  $O_2$  ( $k \sim 10^9-10^{10} M^{-1}s^{-1}$ ) (36) must be avoided. While triplet thionine appears to be insensitive to interaction with solvent or other solutes in a degradative manner, although

detailed studies directed toward that issue have not been conducted,  $^*Ru(bpy)_3^{2+}$  has been found to engage in temperature-dependent photoanation reactions, albeit with low ( $<10^{-3}$ ) quantum yields (37,38). Although the desirable redox quenching reaction can be made to overwhelm energy wastage modes, the existence of even a very low residual quantum yield ( $\sim 10^{-6}$ ) of these degradative reactions can render the photochemical system useless for the required operation over many million cycles.

The parameters affecting the values of  $k'_q$ , the rate constant of redox quenching, have been the subject of increasing numbers of studies with the conversion of light energy into chemical energy as one of the underlying interests. Rehm and Weller (39) have discussed in detail the kinetic and thermodynamic aspects of the quenching process and have derived relationships between  $k'_q$  and the overall free energy change of the excited state reaction;  $k'_q$  increases as  $\Delta G_q^0$  becomes more negative reaching a plateau value at very negative  $\Delta G_q^0$  values corresponding to the diffusion-controlled limit. Other approaches have used the Marcus theory of outer-sphere electron transfer reactions (40) which predicts an inverted region where  $k'_q$  drops from the plateau value when  $\Delta G_q^0$  becomes very negative. "Vestiges" of the inverted region have been found in the quenching of  $^*Ru(bpy)_3^{2+}$  (41) but not in the quenching of triplet thionine (42). Irrespective of the intricacies of these theories, the analysis performed above shows that for short-lived excited states ( $\tau_R^0 \sim 10^{-6}$  s), reaction with  $k'_q$  at or near the diffusion-controlled limit is necessary for efficient conversion of  $^*R$  to separated charge carriers. Therefore,  $\Delta G_q^0$  must be very negative and knowledge and control of the redox potential of  $^*R$  is required. One important consequence of electronic excitation is the increase of the electron affinity and decrease of the ionization potential of the molecule. Therefore, the electronically excited state is expected to be both a better reductant and a better oxidant than the ground state. By assuming that differences in shape, size, solution, and entropy of the ground and excited states are small, the redox potentials of the excited state are fairly well approximated by equations 5 and 6 (43).

$$E^0(M^+ / ^*M) = E^0(M^+ / M) - E_{o-o}^*(M^- / M) \quad (5)$$

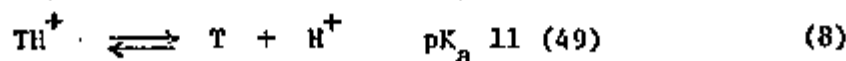
$$E^{\circ}(*M/M^-) = E^{\circ}(M/M^-) + E_{0-0}(M^*-M) \quad (6)$$

Here  $E^{\circ}(M^+/M)$  and  $E^{\circ}(M/M^-)$  are the standard reduction potentials of the one-electron oxidation product and the ground state, respectively, and  $E_{0-0}(M^*-M)$  is the one-electron potential corresponding to the zero-zero spectroscopic energy of the excited state. Potentials are, of course, affected by acid-base reactions of the ground and excited states so that  $k_q^1$  can have pH dependences of consequence. Excited state potentials can also be evaluated from quenching measurements using a series of quenchers of known potentials (44). For  $\text{Ru}(\text{bpy})_3^{2+}$  where  $E_{0-0}(M^*-M) = 2.12\text{V}$ ,  $E^{\circ}(M^+/M) = -0.84\text{V}$  and  $E^{\circ}(M^*/M^-) = +0.84\text{V}$ ; in comparison,  $E^{\circ}(M^+/M) = +1.26\text{V}$  and  $E^{\circ}(M/M^-) = -1.28\text{V}$  (34). Variation of substituents on the polypyridyl rings, including hydrophobic groups, can alter the values of  $E^{\circ}$  by as much as 0.3V (27,34) which can result in variations of  $k_q^1$  of more than a factor of 10 when below the diffusion-controlled plateau (45).

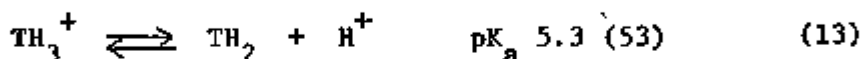
The value of  $k_q^1$  for  $*\text{Ru}(\text{bpy})_3^{2+}$  can also be varied by the solution medium. Meisel and coworkers (46) have shown that incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  into sodium dodecyl sulfate micelles increases the rate of  $k_q^1$  for  $\text{Cu}^{2+}$  by a factor of two. This effect is modest compared to the factor of 2000 increase in  $k_q^1$  when polyvinylsulfate is present in the solution (47). Here, very efficient quenching of  $*\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{Cu}^{2+}$  occurs in the potential field domains of the polyelectrolyte; a similar effect is seen for quenching by  $\text{Fe}^{3+}$  (48).

The redox potentials of both the ground and lowest triplet states of thionine are pH dependent because of the participation of these states, as well as the semi-reduced and fully-reduced species, in rapid, reversible protonic reactions. Relevant  $\text{pK}_a$  values in aqueous solution are given in equations 7-13. The dependence upon pH of the

ground state thionine





triplet thioninesemithionineleucothionine

ground state two-electron reduction potential (vs NHE) in aqueous solution at 25°C is given by equation 14 (53) where T and L represent the sums of all forms of thionine and leucothionine, respectively. The equilibrium potentials

$$E_{T \rightarrow L}^{o'} = 0.563 - 0.09 \text{ pH} + 0.03 \log([T]/[L]) \quad (14)$$

of the two one-electron couples at pH2 in water are  $E_{T \rightarrow S}^{o'} = 0.192\text{V}$  and  $E_{S \rightarrow L}^{o'} = 0.575\text{V}$  (54). The reduction potential for the  ${}^3\text{T}/\text{S}$  couple at pH2 can be estimated from  $E_{T \rightarrow S}^{o'}$  and  $E_{O-O}(T-{}^3\text{T})$ ; this latter quantity for  ${}^3\text{TH}_2^{2+}$ , the predominant form of triplet thionine at pH2, is  $1.2 \pm 0.1\text{V}$  (55) (compared with  $E_{O-O}$  for  $\text{TH}^+ = 1.7 \pm 0.1\text{V}$ ). The result is  $E_{T \rightarrow S}^{o'} = 1.4 \pm 0.1\text{V}$  at pH2.

The intrinsic lifetime of triplet thionine is dependent on its state of protonation. In dilute aqueous solution at pH2, where  ${}^3\text{TH}_2^{2+}$  predominates,  $\tau^o = 7.7 \mu\text{s}$  (31) while in neutral solution, where  ${}^3\text{TH}^+$  predominates,  $\tau^o \sim 60 \mu\text{s}$  (56). The value of  $\tau^o$  of  ${}^3\text{TH}_2^{2+}$  remains essentially constant when the solvent is changed from water to 50 v/v% aqueous  $\text{CH}_3\text{CN}$  and the counter ions are changed from  $\text{HSO}_4^-/\text{SO}_4^{2-}$  to  $\text{CF}_3\text{SO}_3^-$  (31). The lifetime of the protonated form of triplet methylene blue ( ${}^3\text{MBH}^{2+}$ ) has been examined over a wider range of conditions (31) and has been found to be essentially constant ( $4.5 \pm 0.5 \mu\text{s}$ ) in water and 50 v/v% aqueous  $\text{CH}_3\text{CN}$  in the presence of 0.1 - 0.001 M acid, with  $\text{HSO}_4^-/\text{SO}_4^{2-}$ ,  $\text{CF}_3\text{SO}_3^-$ , or  $\text{Cl}^-$  (57) as counter ions, and at ionic strengths between 0.1 and 1.0 M.

The values of  $k'_q$  for the quenching of  ${}^3\text{TH}^{2+}$  and  ${}^3\text{MBH}^{2+}$  by  $\text{Fe}_{\text{aq}}^{2+}$  are sharply dependent on the nature of the counter ions and, in the presence of  $\text{HSO}_4^-/\text{SO}_4^{2-}$  (but not  $\text{CF}_3\text{SO}_3^-$ ) upon solvent (31). For  ${}^3\text{TH}^{2+} + \text{Fe}_{\text{aq}}^{2+}$ ,  $k'_q = 6.0 \pm 0.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  in both water and 50 v/v% aqueous  $\text{CH}_3\text{CN}$  with  $\text{CF}_3\text{SO}_3^-$  as the counter ion but is  $6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  in water and  $5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  in 50 v/v% aqueous  $\text{CH}_3\text{CN}$  with  $\text{HSO}_4^-/\text{SO}_4^{2-}$  as the counter ion. Values of  $k'_q$  for  ${}^3\text{MBH}^{2+} + \text{Fe}_{\text{aq}}^{2+}$  are about 15% of the above values under identical conditions. The observed dependences of  $k'_q$  on solution medium are rationalized in terms of the electrostatic association of  $\text{SO}_4^{2-}$  with  $\text{Fe}_{\text{aq}}^{2+}$  and/or the dipositive dye cations (31). The high sensitivity of  $k'_q$  of the triplet dye molecules to the nature of the solution medium, coupled with the insensitivity of their intrinsic lifetimes, makes it possible to adjust conditions for optimum quenching of the reactive excited states. For example, in 50 v/v% aqueous  $\text{CH}_3\text{CN}$  in sulfate medium at pH2, 97.5% of  ${}^3\text{TH}^{2+}$  and 76% of  ${}^3\text{MBH}^{2+}$  is quenched by 0.01M  $\text{Fe}_{\text{aq}}^{2+}$ . In order to take advantage of the much longer values of  $\tau^0$  for the deprotonated triplet states,  ${}^3\text{TH}^+$  and  ${}^3\text{MB}^+$ , the use of quenchers are required which, unlike  $\text{Fe}_{\text{aq}}^{2+}$ , are compatible with neutral or alkaline solution. Such quenching reactions are under investigation in our laboratory at the present time.

It is clear that conditions can easily be arranged such that the efficiency of quenching of the reactive excited state is virtually unity. The bimolecular quenching of an excited state can occur via electron transfer, energy transfer, or deactivation by some catalytic action and it is only the redox mode that can lead efficiently to the separated charge carriers. Catalytic deactivation processes are generally slow (58) so that the most important modes are electron and energy transfer. As long as the electronic energy requirement of the acceptor is less than the energy available from the donor, energy transfer is thermodynamically allowed; spin restrictions may cause the reaction to be kinetically hindered. It is only by the direct observation of the products of the reaction, redox or excited, that evaluation of the proportion of each process can be made. From the standpoint of energy conversion, it is essential that the efficiency of the redox process,  $\eta_{\text{redox}}$ , be as close to unity as possible. The reaction of triplet thionine with  $\text{Fe}_{\text{aq}}^{2+}$  yields semithionine, the one-electron reduction product, essentially

quantitatively as determined by flash photolysis (56).

For  $^*Ru(bpy)_3^{2+}$ , it is now well established (43) that oxidative and reductive quenching leads to the virtually quantitative generation of  $Ru(bpy)_3^{3+}$  and  $Ru(bpy)_3^+$ , respectively, and the corresponding reduced and oxidized forms of the quencher. Depending upon the nature of the quencher, the derived product can be a stable oxidation state of a metal complex or an unstable free radical. The yield of these separated charge carriers depends upon the fraction of the redox component of the quenching step ( $\eta_{redox}$ ) and the efficiency of separation of the species from their initially formed solvent cage ( $\eta_{sc}$ ); for  $^*Ru(bpy)_3^{2+}$ ,  $\eta_{redox} \sim 1$  (32). Because the products of electron transfer quenching are high energy species, they can engage in immediate back electron transfer in the successor complex within the solvent cage. The critical parameters in the establishment of  $\eta_{sc}$  are the rate of breakdown of the solvent cage and the rate of cage recombination. The factors that govern the events in the solvent cage have been discussed (59); micelles (46) and polyelectrolytes (60) have been used to alter the structure of the solvent cage which causes the yield of solvent separated charge carriers to be altered.

There have been a few determinations of the total quantum yields of formation of the separated charge carriers ( $\phi_{cc}$ ) from the oxidative quenching of  $^*Ru(bpy)_3^{2+}$ . The quenchers have been Co(III) complexes which, upon reduction by  $^*Ru(bpy)_3^{2+}$ , undergo rapid spin equilibration (61) and ligand labilization (62) in competition with cage recombination. For example,  $\phi_{cc}$  values for the formation of  $Co_{aq}^{2+}$  from  $Co(C_2O_4)_3^{3-}$  (63) and  $Co(NH_3)_5Cl^{2+}$  (64) are  $\sim 0.85$ . In general, for Co(III) complexes (65),  $\phi_{cc}$  appears to be between 0.5 and 1.0. However, because of the irreversible nature of the reduction of these and analogous Co(III) systems, their utilization in reversible photogalvanic cells is not practical (66).

What are required are experiments involving the fast generation of  $^*Ru(bpy)_3^{2+}$ , triplet thionine, or any other potential reactive excited states by laser flash photolysis and the quantitative determination of the spectra of the redox products before any appreciable back electron transfer takes place in the bulk solution. In that way,  $\phi_{cc}$  can be determined for the relevant photogalvanic chemical

systems and controlled by means of the alteration of solution medium.

#### Behavior of the Separated Charge Carriers

The quantum yield of separated charge carriers can be expressed in terms of the efficiencies of the various processes that lead ultimately to their formation (equation 15). We have seen that for thionine and  $\text{Ru}(\text{bpy})_3^{2+}$ ,

$$\phi_{\text{cc}} = \phi_{*R} \eta_q \eta_{\text{redox}} \eta_{\text{sc}} \quad (15)$$

$\phi_{\text{cc}} \sim 1$  for semithionine and  $\text{Ru}(\text{bpy})_3^{3+}$  or  $\text{Ru}(\text{bpy})_3^+$ . If these species and the complementary products from the quenching step were capable of diffusing to the appropriate electrodes without engaging in further reaction, a successfully efficient photogalvanic cell would have already been created. It is, however, the necessity of preventing back electron transfer reactions between energy-rich species in bulk solution that challenges the ingenuity of chemists. It is important that thermal back electron transfer reactions be slow compared to the diffusion of the species to the electrodes and electron transfer processes thereon even in order to achieve storage in microtime and transduction of light into electricity. The options for achieving practical photogalvanic storage would be enormously broadened if the rate of thermal back reactions were measurable in hours or days. Some variation in the rate of bulk back electron transfer can be achieved by molecular manipulation of the redox couple and variation of solution medium. Perhaps a more effective way to reduce back electron transfer is to build in an alternative pathway which diverts one or both of the products of the redox quenching. Although contributing to some energy loss, such a diversion can be achieved through other bimolecular reactions or interaction at an interface.

An interesting example of successful competition with prompt reversal of the photoredox step occurs with semithionine which undergoes bimolecular disproportionation to thionine and leucothionine in competition with bimolecular back electron transfer with  $\text{Fe}_{\text{aq}}^{3+}$  generated in the redox quenching step of the iron-thionine photogalvanic cell. The rate constants of these bimolecular reactions are somewhat dependent on solution medium so that it is possible to employ solvent and counter ions to maximize

the disproportionation. Rate constants for disproportionation of semithionine typically fall in the range of  $10^7 - 10^9 \text{ M}^{-1}\text{s}^{-1}$  and, in fact, have been correlated quantitatively with Kosower's solvent parameter,  $Z$  (67). Less is known about the variation of the second-order rate constant for the oxidation of semithionine by  $\text{Fe}_{\text{aq}}^{3+}$  with solution medium. Values in the range  $2 \times 10^4 - 9 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  have been reported at pH2, depending on both solvent and counter ion (24). Conditions are, therefore, readily available for reducing the prompt back electron transfer reaction to a negligible level. Diversion via disproportionation is a promising means of obtaining charge carriers which are stable in the microtime domain because of two factors: 1) synproportionation, the reverse of disproportionation, is much slower than the latter process: the rate constants of synproportionation are of the order of  $10^2 - 10^3 \text{ M}^{-1}\text{s}^{-1}$ , depending on solution medium (54); 2) oxidation of leucothionine by  $\text{Fe}_{\text{aq}}^{3+}$  is much slower than the oxidation of semithionine by this reagent; the rate constants of the leucothionine +  $\text{Fe}_{\text{aq}}^{3+}$  reaction are in the range  $3 \times 10^2 - 2 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  depending on solution medium (24). Leucothionine is, accordingly, the dominant reduced dye species in photobleached iron-thionine solutions under conveniently achieved conditions (7,54). At the photostationary state under sunlight intensities, leucothionine constitutes more than 99% of reduced dye (7). The lifetime of leucothionine under these conditions, determined by measuring the rate of relaxation of the photostationary state, varies inversely with the dark concentration of dye and is dependent upon solution medium;  $\tau \sim 1 \text{ s}$  when  $[\text{TH}^+]_0 \sim 10^{-3} \text{ M}$  in 50 v/v% aqueous  $\text{CH}_3\text{CN}$  at pH7 with  $\text{HSO}_4^-/\text{SO}_4^{2-}$  as counter ion (13). Such a lifetime is sufficient to permit diffusion of virtually all photogenerated charge carriers to diffuse to the electrodes in TI-TL photogalvanic transducers (16). Extension of this classical but nevertheless, promising system from effective storage in microtime toward storage in macrotime may evolve from research involving modification of the structure of the thionine, use of other classes of redox dyes, use of metal complexes other than those of iron, variation of the ligands around the metal center, variation of solution medium, and use of organozates.

$\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{Ru}(\text{bpy})_3^+$  are very powerful one-electron oxidizing and reducing agents with standard reduction potentials of +1.26 and -1.28V, respectively. As a result,

their back electron transfer reactions are very rapid with  $k \sim 10^7-10^9 \text{ M}^{-1}\text{s}^{-1}$  (34) and their storage capability is negligible even in microtime. Furthermore,  $\text{Ru}(\text{bpy})_3^{3+}$  is kinetically unstable in aqueous solutions that are anything except highly acidic; the reduction, which generates  $\text{O}_2$  over a very narrow pH range in alkaline solution, is mechanistically very complicated (68).  $\text{Ru}(\text{bpy})_3^+$  is stable in deaerated acetonitrile solution where it can be generated electrochemically in the controlled-potential reduction of  $\text{Ru}(\text{bpy})_3^{2+}$  (69) but it is unstable in aqueous medium, apparently undergoing slow ( $k \sim 0.2 \text{ s}^{-1}$ ) inter-action with water (70). The instabilities of  $\text{Ru}(\text{bpy})_3^+$  and  $\text{Ru}(\text{bpy})_3^{2+}$  in aqueous solution restrict their use as charge carriers in aqueous photogalvanic cells; investigations of their roles in non-aqueous cells should be carried out in the future. Even so, long-term storage of  $\text{Ru}(\text{bpy})_3^+$  may not be feasible because of its disproportionation reaction to  $\text{Ru}(\text{bpy})_3^0$  although the latter species may be kinetically more stable due to the two-electron nature of its return to the originally absorbing substrate. Back electron transfer involving  $\text{Ru}(\text{bpy})_3^{2+}$  has been shown to be effectively retarded by several orders of magnitude by the presence of polyvinylsulfate (60) and research will certainly continue in that direction. The use of hydrophobic ligands in Ru(II) complexes, monolayer assemblies, and liquid-solid interfaces has been directed toward  $\text{H}_2$  formation (71) but its applicability for photogalvanic conversion should be recognized.

### CONCLUSIONS

It is readily seen that the value of  $\phi_{\text{CC}}$  is not the limiting photochemical determinant of the efficiency of photogalvanic cells but that the storage of separated charge carriers in microtime and macrotime domain is the compelling challenge. There is no question that research will continue for some time to come on quenching reactions, cage recombination, and the chemistry of the charge carriers for systems closely related to thionine and  $\text{Ru}(\text{bpy})_3^{2+}$ . Perhaps those investigations will produce insight into the design of more complex and more successful photogalvanic systems. Solution of the back electron transfer problem is absolutely essential and should involve basic research investigations into the construction of systems where highly exergic electron transfer reactions

can be rendered slow, even in the microtime domain. Novel means must be sought of diverting the immediate products of the redox quenching step via pathways, such as disproportionation, which produce separated charge carriers stable in the microtime, and even macrotime, domain. Such diverted species will be two-electron transfer species; theories of two-electron transfer must be developed to the same level of understanding as those of one-electron transfer. Potential charge carriers can be generated by radiolytic or electrolytic techniques so that their chemistry can be investigated in the absence of photochemical constraints; discovery of kinetically stable charge carriers would then lead to attempts to create the photochemical conditions such that  $\phi_{cc} \rightarrow 1$ . Research programs for the application of the techniques of interfacial chemistry to photogalvanic cells should provide many answers to the problem.

Naturally, the quest for new photochemical systems which can be used in photogalvanic cells must continue. The potentiality of Ru(II)-polypyridyl complexes for solar energy conversion has led to increased interest in polypyridyl complexes of other transition metals. The disadvantages of the very short lifetimes ( $10 \sim 20 \mu s$ ) of  $^*Fe(bpy)_3^{2+}$  (72) and  $^*Os(bpy)_3^{2+}$  (34) in aqueous solution may be offset by advantages in energetics and kinetics;  $^*Os(bpy)_3^{2+}$  is a better reducing agent but a weaker oxidizing agent than is  $^*Ru(bpy)_3^{2+}$  and  $Os(bpy)_3^{2+}$  is a weaker oxidizing agent than  $Ru(bpy)_3^{2+}$  (34). Furthermore,  $Os(bpy)_3^{2+}$  absorbs strongly ( $\epsilon > 10^3 M^{-1}cm^{-1}$ ) in the 300-700 nm region (68) which makes it an attractive light harvesting material. Although  $Cr(bpy)_3^{3+}$  does not absorb strongly ( $\epsilon < 10^3 M^{-1}cm^{-1}$ ) at  $\lambda > 400nm$ , its lowest excited state, which is a metal-centered doublet, has a lifetime in aqueous solution of  $63 \mu s$  (73) which can be prolonged by up to a factor of ten by altering the solution medium or incorporating phen ligands (74).  $^*Cr(bpy)_3^{3+}$  is a much better oxidizing agent than is  $^*Ru(bpy)_3^{2+}$  and undergoes facile reductive quenching (75) in competition with rather complex photochemistry (76). The very low  $E_{0-0}(M^*N)$  value of 1.71V suggests that the absorption spectrum of molecularly modified Cr(III)-polypyridyl complexes can be shifted significantly into the visible.

It is clear that there is a very long way to go before an efficient and economically competitive photogalvanic

cell can be put into operation. Such a goal may never be achieved but it should not be said that this occurred through lack of effort. The studies made in understanding the nature of electron transfer reactions of excited states within this past decade augurs well for the understanding of other factors that comprise the photochemical determinants.

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