

ENERGY BALANCE OF PHOTOREDOX SYSTEMS

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Photochemists have had little motivation for studying energy balances of photochemical reactions. This situation has changed, however, with the interest in the possibilities of photochemical solar energy conversion. The thermodynamic limit for the efficiency of a single photochemical system, operating at 20°C in sunlight, not attenuated by the atmosphere, has been reported to be 29%. Under the same conditions this limit for a converter composed of two systems is 41% [1]. The practical limit for photochemical energy storage is estimated at 15% [2].

The rate of excitation J_e of a system by light in Einstein/sec is equal to the integral over the product of light distribution $I(\lambda)$ (Einstein/sec·cm² [λ]) and absorption cross section $\sigma(\lambda)$ (cm²) of the photosystem.

$$J_e = \int_{\lambda} I(\lambda) \cdot \sigma(\lambda) d\lambda$$

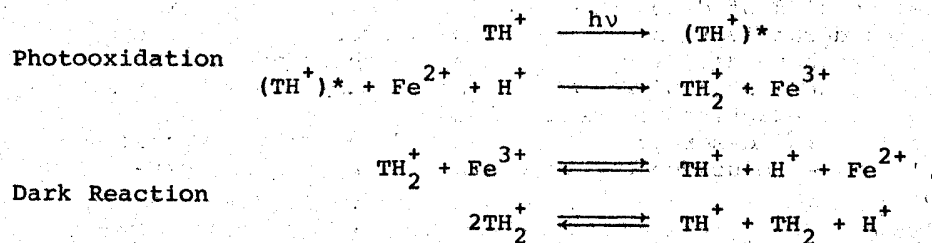
For a process $N^o \xrightleftharpoons{h\nu} N^*$ the thermodynamic potential of the photoproduct in Joule/Mole is approximatively [1]:

$$\Delta\mu^* = RT \cdot \ln \frac{N_{il}^*}{N_d^*}$$

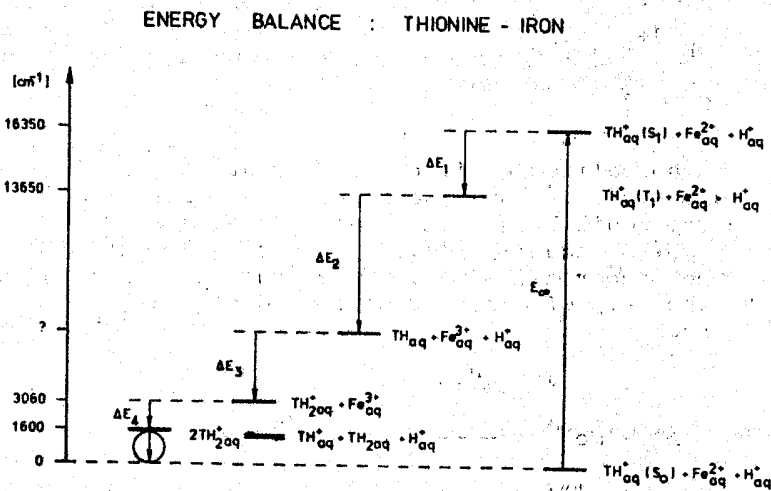
N_{il}^* is the steady state concentration of species in the upper state under irradiation. N_d^* is the concentration of the same state in the dark. The maximum power production P is equal to the flux of photoproducts J_e times the thermodynamic potential of the photoproduct times a loss factor $(1-\phi_{loss})$:

$$P = J_e (1 - \phi_{loss}) \Delta\mu^*$$

There are different methods to get more detailed information on J_e , $\Delta\mu^*$ and on ϕ_{loss} according to the problem to be solved. In the thionine/iron system [3] ϕ_{loss} is well understood [4],[5]. Therefore we shall start with a discussion of this system. Using the abbreviations TH^+ for thionine, TH_2^+ for semithionine and TH_2 for dihydrothionine, the reactions may be summarized with the following scheme:



A detailed energy balance of these reactions is given in Fig. 1:



1 Energy balance of the thionine/iron system

E_{00} is the energy difference between the lowest vibrational level of thionine in the ground state S_0 and in the first excited singlet state S_1 . Changing from the singlet state S_1 to the triplet state T_1 , the excited thionine molecule loses the energy ΔE_1 which is converted to heat*. ΔE_2 is the energy lost during the transfer of an electron from Fe^{2+} to $TH^+(T_1)$. Since the radical TH^* is a strong base, it is immediately protonated. ΔE_3 is equal to the protonation enthalpy ΔH_p° . In a next step two radicals TH_2^* dismutate so that only about 10% of E_{00} can be used to drive e.g. a photogalvanic cell.

This kind of discussion provides useful insight into the different desactivation paths. For many problems, however, it is necessary to have detailed information on the concentration dependence of the system behaviour. We have found that a generalization of the reduction degree introduced by Michaelis [7] is very useful for the description of redox and photoredox systems [4], [8]-[10]. The reduction degree of the thionine/iron system is defined by [4]:

$$r = \frac{[TH^+] + 2[TH_2] + [Fe^{2+}]}{2G_1^\circ + G_2^\circ} \quad ; \quad 0 \leq r \leq 1$$

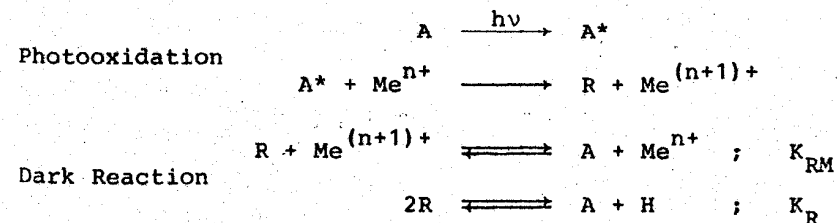
G_1° and G_2° are the total concentrations of thionine and iron respectively:

$$G_1^\circ = [TH^+] + [TH_2^*] + [TH_2]$$

$$G_2^\circ = [Fe^{3+}] + [Fe^{2+}]$$

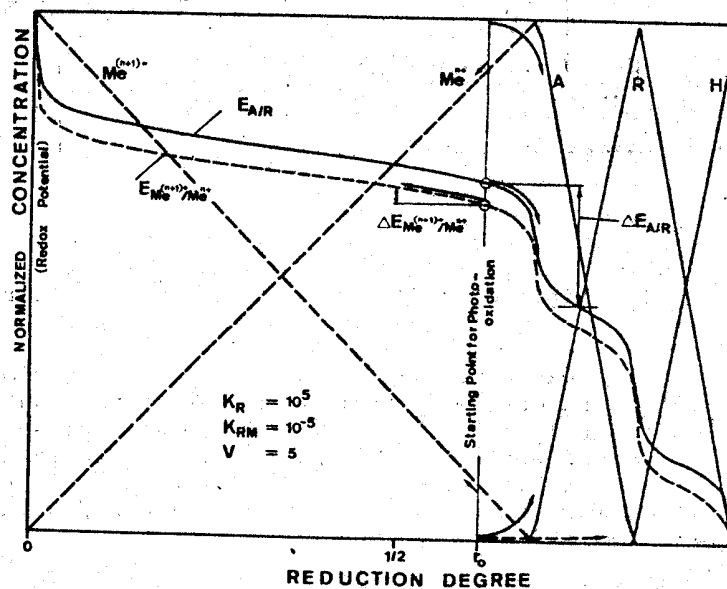
$$v = G_2^\circ / G_1^\circ$$

Figure 2 shows the normalized equilibrium concentrations of a thionine like model system versus the reduction degree. $E_{A/R}$; $E_{Me^{(n+1)+}/Me^{n+}}$ are the equilibrium potentials. Of course, $E_{A/R}$ is equal to $E_{Me^{(n+1)+}/Me^{n+}}$ at equilibrium. For clearness' sake, the two curves have been separated by ΔE . The calculations have been carried out with the help of a method described elsewhere [11]. The model considered is:



* We do not distinguish between the energy of the T_1 and the T_2 states [6].

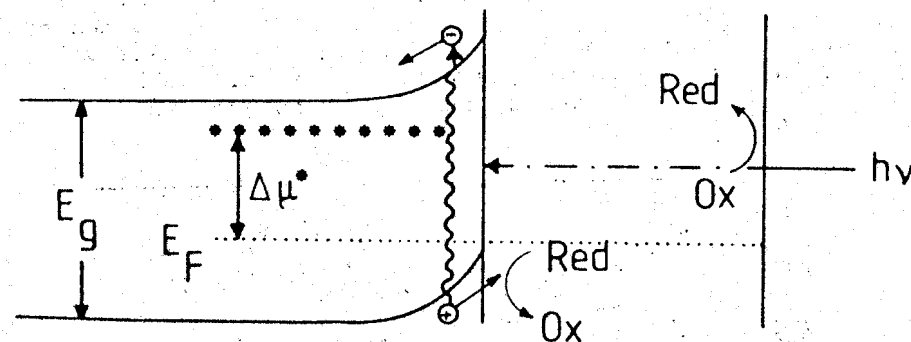
If a sample is irradiated at a fixed reduction degree, the photo-oxidation shifts the individual concentrations from the equilibrium in the directions marked by arrows. r_0 is a particularly interesting point to start the reaction from. Since no reduction equivalents are transferred to or from the system, r_0 remains unchanged. This means that the reduction degree is an invariant under irradiation. Under certain assumptions which are often not very restrictive, it is perfectly possible to calculate all the nonequilibrium concentrations as well as the half cell potentials in rather complex photoredox systems. This subject is discussed elsewhere [10].



2 Normalized equilibrium concentrations and equilibrium potential versus the reduction degree. For the redox potential the total ordinate corresponds to 1 V.

Heterogeneous photoredox systems in which the photosensitive part is a semiconductor material seem to be among the most promising chemical systems for the conversion of light energy into electrical energy [12], [13]. In Figure 3 the principle of a photoelectrochemical cell is shown. By absorption of a photon an electron from the valence band is excited to the conduction band. This creates a potential difference $\Delta\mu^*$ between the redox potential of a redox couple Red/Ox in solution and the semiconductor. A hole created in the valence band can therefore oxidize a Red. By inserting a counter electrode a current between the illuminated electrode and the reference electrode can be observed. The power

production of such a cell depends mainly on $\Delta\mu^*$, the bandgap E_g and the quantum yield for the current (number of electrons produced by 1 Einstein photons absorbed) at a given $\Delta\mu^*$.

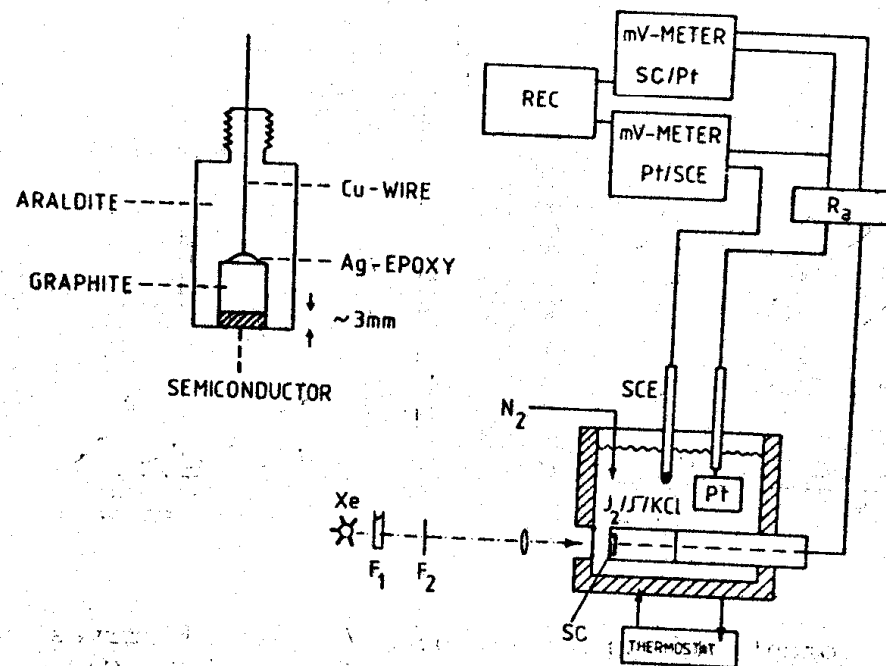


3 Principle of the mechanism of a photoelectric cell.

Figure 4 shows the experimental set-up for the observation of photopotentials and photocurrents we have used to investigate doped sintered $\alpha\text{-Fe}_2\text{O}_3$ in I_2/I^- , KCl solutions [14]. Xe represents a 150 watt high pressure xenon lamp. F_1, F_2 are filters. SC is the semiconductor, Ra a variable resistor and REC a two channel recorder. As homogeneous redox couple we have used the iodine/iodide solutions shown in Table 1:

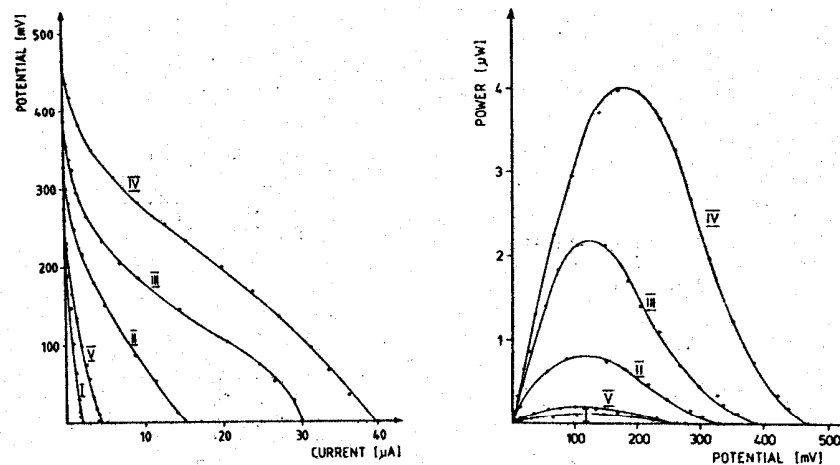
Table 1: Composition of the electrolyte solutions [Mol/l]

| Electrolyte / Number | I | II | III | IV | V |
|--|-----------|-----------|-----------|-----------|-----------|
| I_2 | 10^{-2} | 10^{-3} | 10^{-4} | 10^{-4} | 10^{-3} |
| I^- | 10^{-1} | 10^{-1} | 10^{-1} | 1 | 1 |
| KCl | 1 | 1 | 1 | 1 | 1 |
| Relative transmission for visible light $350 < \lambda < 650 \text{ nm}$ | 43% | 66.2% | 100% | 99.7% | 67.8% |



4 Electrode and experimental set-up for the observation of photopotentials and photocurrents.

From the wavelength dependence of the photopotentials we know that photoactivity of our electrochemical cell starts at the same wavelength (600-650 nm) as the absorption of light of a thin vacuum deposited film. No photocorrosion could be observed in neutral solution. The photopotentials are much higher than we had expected. There is a remarkable dependence of the photoresponse of the iron(III) oxide on the redox electrolyte. The potential/current and the power/potential curves we have observed on iron(III) oxide doped with 10/00 CaO are shown in Figure 5.



5 Potential/current and power/potential curves observed on iron(III) oxide doped with 1% CaO. The numbers I to V refer to Table 1. Electrode surface 1 cm².

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