



2. THEORY

Although a growing interest (1, 16, 25-29) in the possible use of photoelectrochemical effects for the conversion and storage of solar energy commenced with the observations of Bequerel (6) in 1839, photoelectrochemical studies are still at an early stage of development. This is partly due to the complexities introduced into the theory of photoelectrochemical effects by the combination of the diverse fields of photochemistry and electrochemistry and partly due to the storage of reliable data on the electrodic and photolytic properties of the fluorescent dyes commonly used in photoelectrochemical cells.

The following theory is concerned with the general principles of photochemistry and the theoretical considerations of the maximum efficiency for photochemical storage of solar energy. The theoretical maximum power output and the conditions for the most efficient operation of photogalvanic cells are described.

Principles of Photochemistry

Light is composed of a large number of units called photons, each with a definite energy known as a quantum of energy. Only if the molecule can be rearranged to absorb an amount of energy nearly equal to that contained in a given photon does the photon have a chance of being absorbed by the molecule. Absorption of

energy from ultraviolet or visible light is accomplished by displacement of an electron from its normal position in the molecule. In the infrared, the absorption of energy is accomplished by displacement of atoms within the molecule or by rotation of the molecule. Only the electron displacements involve enough energy to provide sufficient activation energy for bringing about ordinary chemical reactions. For sunlight, these extend from the red at about 800 nm to the ultraviolet at about 300 nm, corresponding roughly to 150 kJ mol^{-1} and 400 kJ mol^{-1} .

According to the important Einstein relation, one photon can activate only one molecule. After this activation of a molecule by a photon of visible or ultraviolet light, the following phenomena may occur (31).

1. The light-activated molecule may transmit its energy to other molecules by collision, increasing the translational energy of the molecules and raising the temperature. In this way the radiant energy is converted directly into heat without any chemical changes. This is by far the most common effect produced by sunlight.

2. The activation may break a chemical bond in the molecule and give chemical decomposition into atoms or groups of atoms.

3. The molecule may be activated to a higher energy level by displacement of an electron within the molecule, and this excited molecule may transfer its

energy to a molecule of some other chemical compound with which it collides; and this second molecule may undergo chemical change. In this photosensitization a loose combination between photoactivated molecule and chemically reacting molecule appears to be necessary. Time is required to effect the energy transfer, and the combination holds the two molecules together long enough for the transfer of energy.

4. A molecule excited by the absorption of light may fluoresce, giving off light of a different wavelength from the exciting light. The energy states of the electrons are different in fluorescent emission and absorption.

5. The activation may have enough energy to drive an electron out of the molecule and produce ionization.

The quantum yield, ϕ is the most important quantity in photochemical measurements. It is defined by the relation

$$\phi = \frac{\text{number of molecules reacting}}{\text{number of photons absorbed}}$$

The amount of reaction depends on the intensity of light, the thickness of the absorbing layer, and the concentration, but a knowledge of the quantum yield permits a calculation of the amount of chemical change

from the amount of light absorbed under a variety of conditions.

The quantum yield is also of theoretical importance. Although there can be no photochemical reaction if there is no absorption of light, and although each photon of light absorbed activates one, and only one, molecule, the quantum yield varies greatly in different reactions because the chemical reactions that follow photoactivation are complicated. If ϕ is large a chain reaction must be taking place involving many molecules; if it is small (less than unity) several possibilities may be involved such as the reversal of the photochemical reaction, loss of activation as heat, competition with other reacting molecules, or internal absorption of light by other molecules which absorb the light but do not produce the given reaction.

The criteria for selecting photochemical reactions of possible value in utilizing solar energy are as follows:

1. The photochemical reaction produced by sunlight must be endergonic (energy absorbing) with a high quantum yield.

2. In order to use the stored photochemical energy the reaction must be reversible, and the reverse reaction must be fast enough to be practically useful but

not so fast that the reverse reaction is complete during the time of exposure to the light.

3. The reactants, or a photosensitizer, should absorb light throughout most of the visible spectrum to use photochemically as much as possible of the total solar radiation. There is almost no chance that the infrared half of the sunlight can be used photochemically because the energy per photon is too low to bring about chemical reactions.

4. For the direct conversion of solar energy into electrical energy the electrons are transferred photochemically from a position of lower energy to a position of higher energy. If they return to the position of lower energy instantly no energy can be stored.

5. Liquids and solids are preferred as reactants because of their smaller size, but reactions involving gases are also worthy of consideration.

6. The quantum yield for the production of photoproducts should be as high as possible.

There are several ways in which the energy produced in these photochemical reactions may be stored and used.

1. The photoproducts may be separated and stored indefinitely for use at a later time. For a gaseous

product, it may be insoluble and automatically evolved from a liquid solution containing the reactants; or solid products may be precipitated from solution. In another method the photochemical products can be separated by dissolving each in a different liquid solvent using solvents that do not mix with each other.

2. Sunlight can be used as work more effectively if the stored energy is released as electrical energy rather than as heat.

3. If the reactants respond only to the short wavelengths of sunlight in the ultraviolet and blue, the range of usefully absorbed light may sometimes be extended to longer wavelengths by making structural changes in the molecule. The absorption bands of organic dyes can be shifted toward the red by incorporating heavier atoms or groups of atoms into the molecule. Photosensitizers may also be used to extend the range of photochemically active absorption.

4. The photoproducts may be kept separate and stored by using a two-phase system such as a pair of immiscible solvents or the two parts of an electrochemical cell.

5. Photochemical storage of sunlight can be carried out in solids as well as in liquids, solutions and gases.

Maximum possible efficiency for the photochemical storage of solar energy

Bolton (31,32) stated the limit on efficiency for the photochemical storage of solar energy which can be considered from a reaction,



where R is the absorber and P is the primary product of the photochemical step.

A general representation of this endergonic photochemical step is shown in Figure 4.

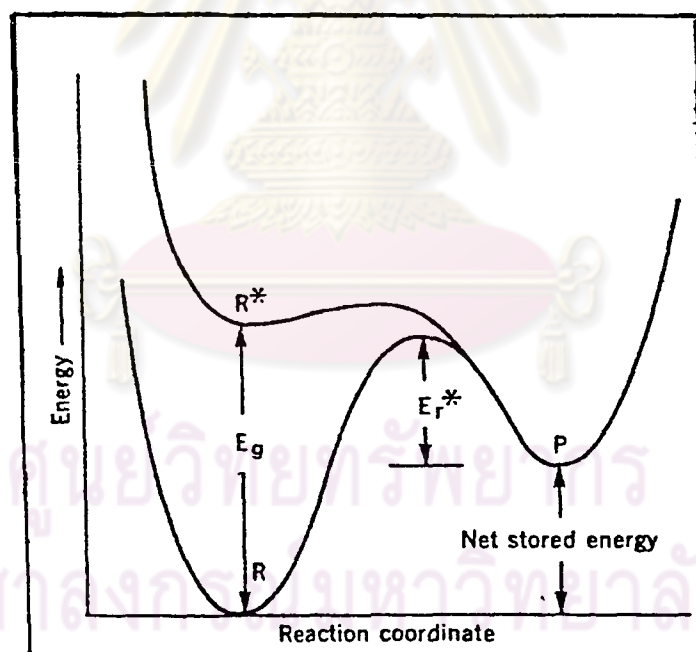


Figure 4. Energy profile for a general endergonic photochemical reaction $R \rightarrow P$; E_g is the minimum energy gap between the lowest vibrational levels of the excited state R^* and the ground state of R , and E_{r^*} is the activation energy for the back reaction $P \rightarrow R$.

The reaction may involve more than one reactant, but the overall process will be considered to be first order. There are three fundamental energy losses which must be incurred for any photochemical energy:

1. Photons having a wavelength λ such that $\lambda \geq \lambda_g$, where λ_g is the wavelength corresponding to the energy E_g (Figure 4), do not have sufficient energy to raise R to R^* and thus cannot contribute to the photochemistry.

2. Photons that are absorbed with $\lambda < \lambda_g$ may raise R to R^* , but the very efficient process of internal conversion will reduce R^* to its lowest vibrational level within a few picoseconds and hence the excess photon energy above E_g will be lost as heat (Figure 5).

3. The conversion R^* to P must be exergonic because if p is to have a reasonable lifetime, then an activation barrier must be built in for the back reaction P to R^* . Such an activation barrier can be activated only with the loss of some of the excitation energy of R^* as heat.

The analysis of the maximum possible efficiency is usually made with the following assumptions:

1. Every photon of light absorbed will contribute towards the production of P from R . That is, the quantum yield for the production of P will be assumed to be 1.0.

2. All photons with wavelengths less than λ_g will be absorbed.

3. λ_g will be taken as 700 nm since there are very few photochemical reactions with λ greater than 700 nm.

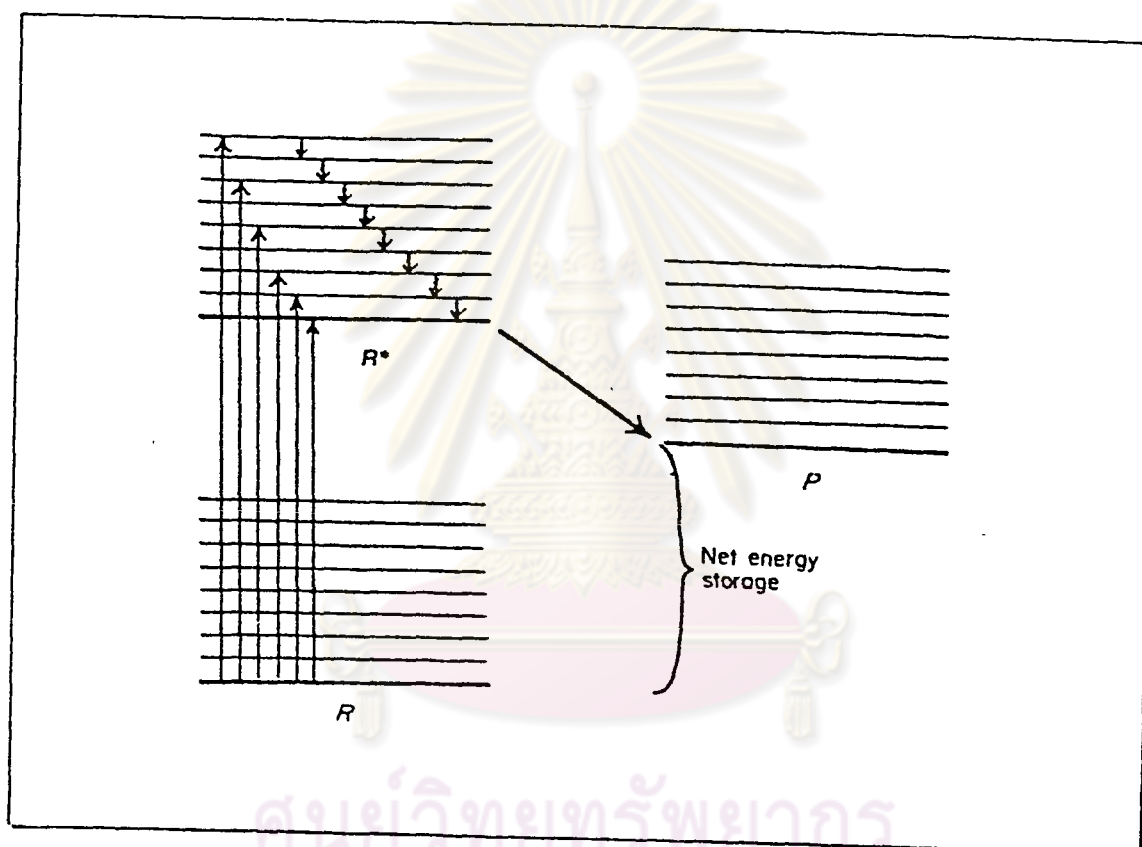


Figure 5. Energy level diagram corresponding to the photochemical reaction $R \rightarrow P$.

4. The solar spectrum will be taken of air mass (AM) 1.2 (a bright sunny summer day near noon) (33) with a spectral distribution curve as shown in Figure 6. Thus at least 52 percent of the solar spectrum is lost in the first loss term.

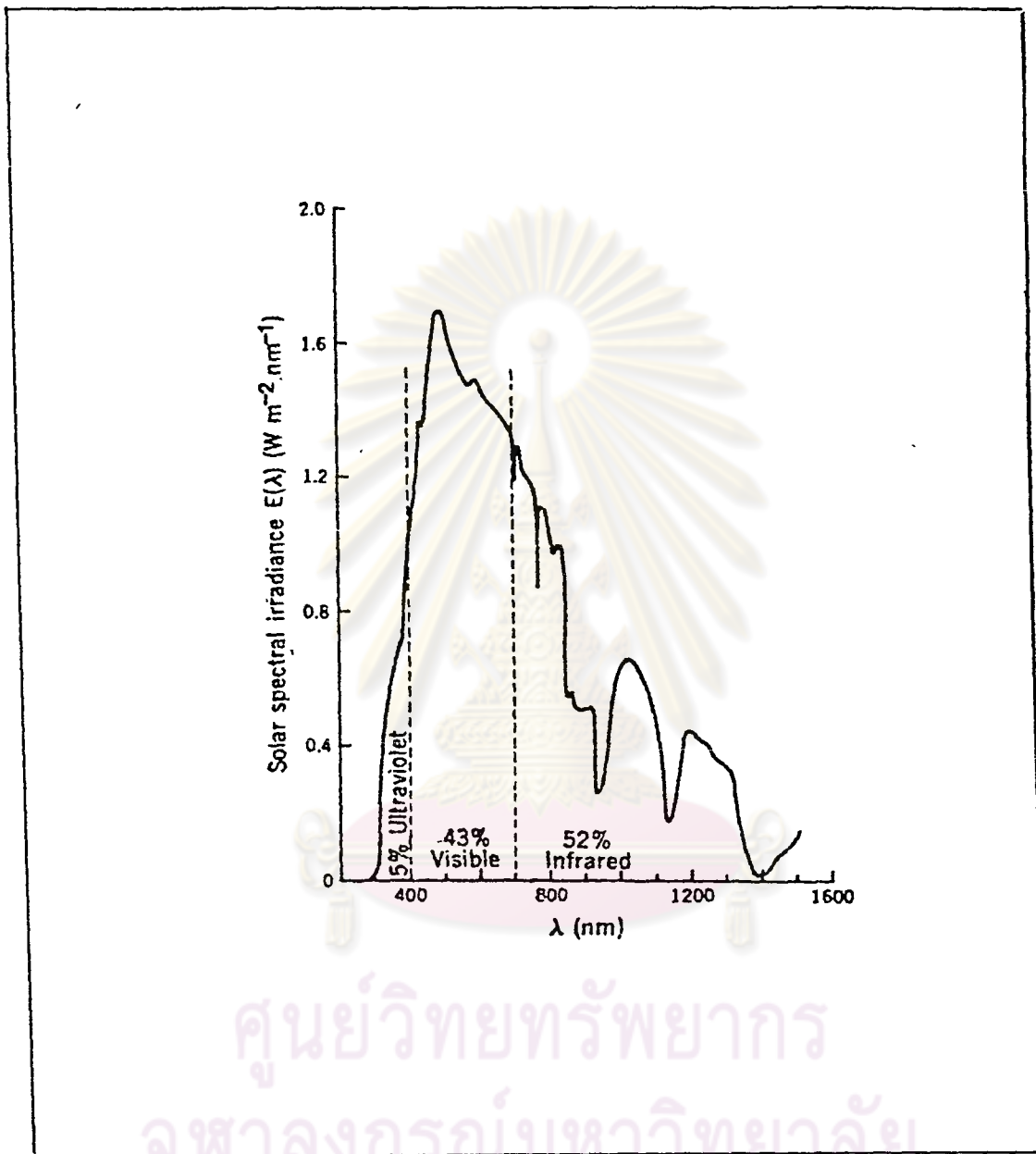


Figure 6. Solar spectral distribution for AM 1.2. The spectrum is shown only out of 1500 nm; however, the 52 percent for the infrared portion of the spectrum refers to the total integrated irradiance for $\lambda > 700$ nm.

5. The energy loss in the reaction R^* to P will be taken as 52 kJ mol^{-1} . That is, the activation barrier for the reaction P to R^* will be assumed to be 52 kJ mol^{-1} . This value corresponds to a 30 percent loss of energy in the reaction R^* to P.

With the above assumptions, the energy losses calculated for 10 nm intervals are

Loss term NO. 1	52	%
Loss term NO. 2	13.5	%
Loss term NO. 3	11.8	%
	<hr/>	
	77.3	%

Hence, the maximum possible efficiency under the above assumptions is 22.7 percent.

Of course, a real system will incur further losses due to:

1. Incomplete absorption of sunlight with wavelengths less than λ_g

2. Loss of some photons due to fluorescence, internal conversion to the ground state, side reactions, etc. A real system is unlikely to exhibit a quantum yield of greater than 0.90.

3. The activation barrier for the reaction P to R^* in a real system is likely to be greater than the 52 kJ mol^{-1} assumed above, especially if more than one step is involved. A value of 70 kJ mol^{-1} or an energy loss of

40 percent in the reaction R^* to P may be more reasonable.

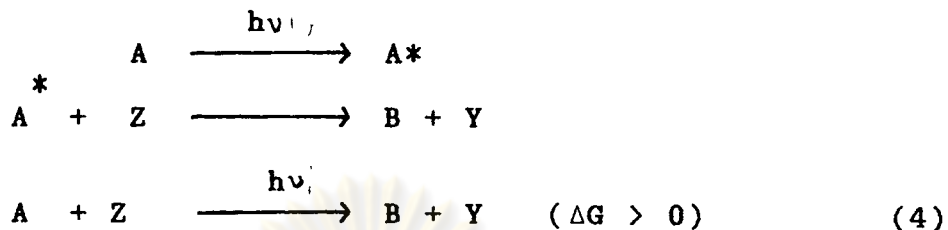
When these three terms are accounted for the energy storage efficiency drops to 15.9 percent. Hence, an efficiency of 15-16 percent represents a realistic maximum efficiency for a photochemical solar energy storage system.

A type of photochemical solar energy storage systems, the photogalvanic cell, is also subject to the above limitations but up to now there is no special rule describing the behavior and mechanism of the components of such cells. The variation of the power output and the conditions for the most efficient operation of the cell will be considered below.

The reaction scheme of photogalvanic cell

Since the electrochemical cell reaction in a power-producing photogalvanic cell must be spontaneous and must represent net conversion of radiant energy to electrical energy, it follows that only an endergonic photochemical reaction may be made as the basis of a photogalvanic cell. The general reaction (1,16,25) for a photogalvanic cell involves two redox couples A, B and Y, Z, dissolved in an electrolyte. One component, A, is a dye that absorbs the solar radiation, whereupon the excited A^* undergoes an electron-transfer reaction with Z

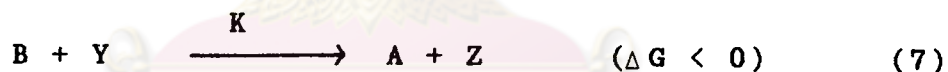
to form two energetic products, B and Y. The photoredox process occurring in the solution is represented by:



The redox couples, A/B and Y/Z, occurred at the electrodes (so-called electrode reactions) are represented by:



The cell reaction should ideally be the reverse of (4):



and should occur only at the electrodes. However, this is a spontaneous process, and it can and generally does occur also in homogeneous solution before B and Y can diffuse to, and react at, the electrodes; this homogeneous back reaction may greatly reduce the cell efficiency.

If the back reaction occurs sufficiently slowly to allow B and Y to be separated, or so slowly that they could coexist in appreciable concentrations in solution, then the photogalvanic cell would have useful storage

capacity; i.e., radiant energy could be converted to chemical energy on recharge and chemical energy to electrical energy on discharge.

Redox potentials of ground and excited states

Since the redox behavior of a dye in its excited state is governed almost exclusively by the ground state redox potential and the excitation energy, it is important to have information available on the reduction potential of the dye.

Oxidation and reduction potentials are thermodynamic characteristics of redox equilibria; consequently, one might logically question how it is possible to define a reduction or oxidation potential for an excited state. Nevertheless, this concept has found considerable utility in predicting the redox reactivity of excited states (34). Consider the cycles shown in Figure 7 for a photochemical electron donor and an acceptor.

Based on the work of Rehm and Weller (35) on singlet charge-transfer exciplex phenomena, Bock et al. (36) deduced that for a photochemical electron donor:

$$\Delta G = F[E(D^+/D) - E(A/A^-)] + W_p - W_r \quad (8)$$

where F is the Faraday constant, the E^0 are the formal reduction potentials (mid-wave potential at pH7) and W_p and W_r represent the work required to bring the products (D^+ and A^-) and the reactants (D^* and A) together, respectively. W_p can be estimated from the Debye-Huckel

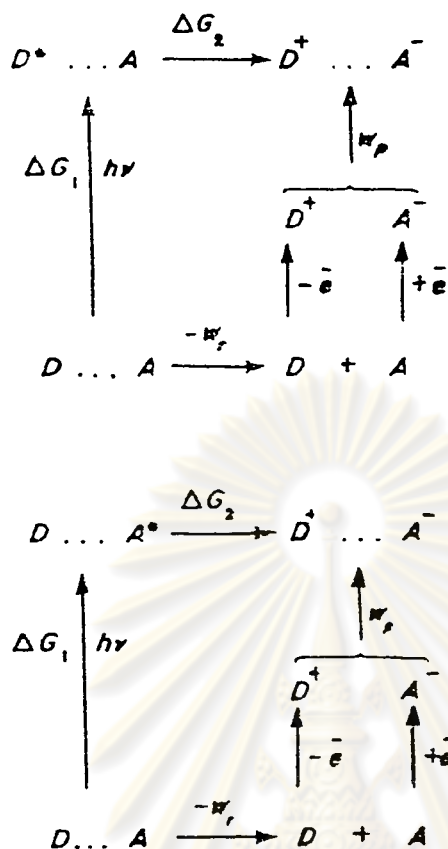


Figure 7. Free energy cycles illustrating the derivation of equations (8) and (10). (a) Cycle for excitation of D, (b) Cycle for excitation of A. In both cycles, it is assumed that $\Delta G_1 \sim E^*$.

theory as 0.026 eV and W is assumed to be negligible. Bock, et al. (36) found that $E' (D/D^+)$ was well represented by what we might call a pseudo reduction potential:

$$E' (D/D^+) = E' (D/D) - (F)^{-1} \Delta E^* \quad (9)$$

where ΔE^* is $E^* - E$ where D is the photoactive excited state of D.

Similarly, for a photochemical electron acceptor (Figure 7(b)):

$$\Delta G_2 = F[E'_0(A/A^*) - E'_0(D/D^+)] + W_p - W_r \quad (10)$$

and

$$E'_0(A/A^*) = E'_0(A/A) + (F)^{-1} \Delta E_A^* \quad (11)$$



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Criteria for the successful photogalvanic cell

Cell efficiency (1), expressed as the ratio of power output at the maximum power point to incident radiant power, depends upon several factors: solution photochemistry and other homogeneous kinetics, mass transport and electrode kinetics.

Electrode kinetics and characteristic lengths of photogalvanic cell

The performance of the cell depends on the kinetics of the electrode reaction (25). On either electrode, either couple can have 'reversible' or 'irreversible' electrode kinetics. When a couple is reversible the electrode kinetics are rapid and the surface concentrations of the couple at the electrode obey the Nernst equation. When a couple is irreversible the electrode kinetics are sluggish and considered to be the extreme case where no electrode reaction takes place. The performance of cells, in which couples have intermediate electrode kinetics, will be between the two extremes that are considered. Four of the 16 possible cases are shown in Table 1.

Eight cases which have irreversible electrode kinetics for both couples on either of the electrodes can be rejected because to pass current it is essential that one of the couples should be reversible on each

electrode. Four cases in which the Y, Z couple is reversible on both electrodes can be rejected

Table 1. Reversible (R) or irreversible (I) electrode kinetics.

couple	Illuminated electrode		Dark electrode		Notes
	A,B	Y,Z	A,B	Y,Z	
Case 1	R	I	R	I	concentration cell
Case 2	R	I	I	R	Differential electrode kinetics I
Case 3	R	I	R	R	Differential electrode kinetics II
Case 4	R	R	R	I	Reject

because it is assumed that the concentrations of Y and Z are large, compared to the concentration of A so that the concentrations of Y and Z throughout the cell are not significantly perturbed from their values in the dark. So if the couple is reversible, the two electrodes will have the same potential and no power is produced. Similarly the fourth case in Table 1 can be rejected because at the dark electrode the reversible A, B couple will give the same potential as the reversible Y, Z couple on the illuminated electrode. This leaves three cases worth considering. In the first, the electrode

kinetics are similar on the two electrodes and hence they can be made of the same material. The cell works as a 'concentration cell'. In the other two cases the electrode kinetics are different on the two electrodes and the cell works with 'differential electrode kinetics'.

To find the power developed by the cell it is necessary to calculate how the concentration of B varies with the distance between the two electrodes. A steady state is established described by the differential equation:

$$D \frac{\partial^2 b}{\partial x^2} + \phi I E a - k b y = 0 \quad (12)$$

where D is the diffusion coefficient of B

x describes the distance from the illuminated electrode

ϕ is the quantum efficiency for the generation of B from A

I is the quantum intensity of the light

E is the natural extinction coefficient of A

a, b, and y are the concentrations of A, B and Y, respectively

The first term describes the diffusion of B, the second term its photochemical generation and the third term the thermal reaction with Y.

In giving the results of the calculations it is convenient to introduce the characteristic lengths given in Table 2.

The maximum power W_{\max} produced by the concentration cell (case 1 in Table 1) can be shown to be

$$W_{\max} = 0.28 ART\phi I_0 \quad (13)$$

where A is the area of each electrode

T is the temperature of the electrolyte

Table 2. Characteristic lengths

Symbol and equation	Description
X_1	Distance between electrodes
$X = E[A]^{-1}$	Distance over which light is absorbed.
$X_k = (D/k[Y])^{1/2}$	Distance over which B diffuses before being converted to A.
$X_g = (D/\phi I_0 E)^{1/2}$	Distance over which A diffuses in light of intensity I_0 before being converted into B.

This is the maximum possible power that can be obtained after optimising the concentrations of the species, the dimensions of the cell and the load on the

cell. The conditions for this maximum are:

$$X_E < X_g < X_k < X_l \quad (14)$$

and

$$X_E^3 = X_k X_E \quad (15)$$

The maximum power produced by a cell with differential electrode kinetics (case 2 or 3 in Table 1) can be shown as:

$$W_{\max} = 0.8AF\phi I_o \left[|\Delta E| + \frac{RT}{F} \left\{ \ln \frac{\phi I_o E}{k[z]} - 1.6 \right\} \right] \quad (16)$$

$$0.8 AF\phi I_o \Delta E \quad (17)$$

where $|\Delta E|$ is the difference in standard electrode potentials for the A, B and Y, Z couples. The conditions for this maximum are:

$$10X_E \approx X_g \approx \frac{1}{2}X_k < X_l \quad (18)$$

For both types of cell the order of the characteristic lengths in equation (14) and (18) are the same. The shortest length must be X_E to absorb all the photons closed to the electrode. The inequality $X_E > X_k$ ensures that B is formed within the distance X_E , is not decomposed by reaction with Y before it reaches the electrode. The conditions for X_E ensure that the solution does not become bleached near the illuminated electrode. The condition for X_l means that the dark

electrode does not interfere with the trapping of the photons and the reaction of B on the illuminated electrode.

Taking $I_0 = 1.6 \times 10^{-3}$ mol photons $m^{-2} s^{-1}$ and $\phi = 1$, we obtain from equation (13)

$$W_{\max} / A = 1.1 \text{ W m}^{-2} \quad (19)$$

This is the maximum power that can be obtained from a photogalvanic concentration cell by solar energy. The power conversion efficiency is no more than 0.2% (1) and we conclude that the concentration cell cannot be an effective device for solar energy conversion.

For a cell with differential electrode kinetics, the maximum power is given by equation (18). Not only is the collection efficiency much closer to unity but also the cell voltage is now given by E rather than the miserable RT/F of the concentration cell. The optimum value of E is 1.1 V. With this value and the same value of I_0 as above we obtain.

$$W_{\max} / A = 140 \text{ W m}^{-2} \quad (20)$$

This corresponds to a power conversion efficiency of 18% (25).