1982

4th INTERNATIONAL CONFERENCE ON PHOTOCHEMICAL CONVERSION AND STORAGE OF SOLAR ENERGY

Hebrew University of Jerusalem, Mount Scopus
August 8—13, 1982
Jerusalem, Israel

PLENARY LECTURE VI

PHOTOGALVANIC CELLS AND EFFECTS

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PHOTOCHEMICAL CONVERSION
AND STORAGE OF SOLAR ENERGY
1982
PART A

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THE WEIZMANN SCIENCE PRESS OF ISRAEL
1982

Transformation of Light Energy into Chemical Energy

III. SOME ASPECTS OF PHOTOGALVANIC CELLS*)

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Summary

Photogalvanic cells are photoelectrochemical devices in which in a homogeneous or a heterogeneous photoreaction products are formed which in a second step can react at appropriate electrodes. Photogalvanic cells have been identified as iron-thionine-like and iron-rutheniumtrisbipyridyl-like systems. This is not generally valid as e.g. in the iron-iodine and in the silver halide case. The necessity to discuss the equilibrium situation carefully has been underestimated, not only with regard to photogalvanic cells but also to many photoredox reactions. This is the reason for discussing equilibrium situations and photostationary states first. It is shown that the reduction degree plays a central role. - We have to conclude that iron-thionine like systems and the iron-iodine system as they are known today cannot contribute to solar energy conversion.

We have found that in presence of Cl^- and Br^-, irradiation of silver zeolites leads to the production of chlorine and bromine within a broad pH range.

$$[Ag^+]_n[Zeol](mCl^-)_{ads} \xrightarrow[>350\ nm]{h\nu} [Ag_n]^{(n-r)+}[Zeol]((m-r)Cl^-)_{ads} + r/2\ Cl_2$$

Some comments on the photoproduction of halogens from silver halides have appeared in the literature. But in general this reaction which leads to a very good storage capacity - Ag,AgCl|HCl(1m)|

*) Part I : Chimia 32, 241 (1978)
Part II: Chimia 35, 209 (1981)

Cl^-, 1/2 Cl_2, $\Delta E° = 1.14$ Volt - has been ignored. The reaction is very interesting from a kinetic point of view. Chlorine remains in solution and should therefore undergo rapid recombination. But the back reaction Ag + 1/2 $Cl_2 \rightarrow AgCl$ is observed to be slow despite of the large driving force, as long as the chlorine concentration is not too high. Therefore, it is very easy to separate the photoproducts, e.g. by filtration or by using the solubility of chlorine and bromine in graphite. This means that energy storage can be achieved. If a silver electrode and a graphite or platinum electrode are immersed in a silver-zeolite suspension containing Cl^-, a potential difference between the silver electrode and the graphite or platinum electrode of about 1 Volt is observed a few minutes after irradiating the system. The silver electrode remains on the Ag/AgCl potential while the counter electrode adopts the Cl_2/Cl^- potential. As soon as enough chlorine has been produced, currents of more than 0.1 mA/cm^2 at up to 700 mV cell voltage can be observed if a resistor of e.g. 1 kΩ is put between the two electrodes. This means that the Ag/AgCl electrode behaves selectively in a similar way as we found the SnO_2 and glassy carbon electrodes in the iodine-iron system do, although there are important differences between the two systems.

During our studies regarding the reoxydation of the photochemically produced silver we have observed the following reactions:

$$[Ag_n]^{(n-r)+}[Zeol]((m-r)Cl^-)_{ads} + u[Cu^{2+}]$$

$$\xrightarrow[\text{160°C}]{Cl^- \text{ solution with } Cu^{2+}} \text{or} \xrightarrow[\text{pH 9.5, 25°C}]{\text{ammoniacal solution}} [Ag_n]^{(n-r+u)+}[Zeol]((m-r)Cl^-)_{ads} + u[Cu^+]$$

Some of the problems related to these systems are mentioned. Trying to improve the iron-iodine system, we have observed very interesting photopotentials with a chromium-iodine system.

I. Introduction

In the first paper of a series[1] W.J. Albery and M.D. Archer have divided photoelectrochemical devices for the direct conversion of solar energy to electrical energy into two categories: those in which a homogeneous photochemical reaction forms products which react at the electrodes, and those in which direct irradiation of the photosensitive electrode or membrane produces charge injection across a phase boundary. The first category has been called photogalvanic cells. There is no reason to exclude heterogeneous systems. But some years ago the iron-thionine and the iron-rutheniumtrisbipyridyl systems have dominated the field. Today we expect from heterogeneous systems the most interesting effects, as I will show. We now define a *photogalvanic cell* as a photoelectrochemical device in which in a homogenous or a heterogeneous photoreaction products are formed which in a second step can react at the electrodes. In semiconductor/liquid systems, in which a semiconductor electrode has necessarily to be illuminated, the primary step can be described as an electron/hole production in the semiconductor electrode. The basic difference between photogalvanic cells and this type of electrochemical cells is that in photogalvanic cells in principle it is not necessary to illuminate an electrode, because the photoreaction takes place in the solution and not at the electrode/solute interface. Of course, direct illumination of an electrode can also in photogalvanic cells often be an advantage for kinetic reasons. Some authors have identified photogalvanic cells as iron-thionine-like and iron-rutheniumtrisbipyridyl-like systems. That is why they have concluded that a photovoltage can only be observed if the incident light is absorbed near an electrode[2]. This is not generally true, as e.g. in iron-iodine reactions[3] and in silver-halide systems[4].

The iron-thionine-like and the iron-$Ru(bipy)_3^{2+}$-like reactions have been studied in detail [5]. The conclusion is that these systems as they are known today cannot be of practical interest for direct conversion of solar energy. It is not my intention to review these studies. This has been done at the two previous conferences 1978 by W.J. Albery[6] and 1980 by M.D. Archer[7]. But let us see what we can learn from these systems by regarding them from a different angle and what the consequences of the extension to heterogeneous systems are.

The necessity to discuss the equilibrium situation carefully has been underestimated - not only with regard to photogalvanic cells but to many aspects of photoredox reactions. This is the reason for starting the following discussion.

II. Equilibrium Situation and Photostationary State

Each photoredox system is composed of at least two independent redox couples. The iron-thionine-like system e.g. consists of the two couples

thionine (TH^+), dihydrothionine (TH_2), semithionine (TH_2^+)
and
Iron(III)/Iron(II),

or in the iron-rutheniumtrisbipyridyl case we have:

$[Ru(bipy)_3]^{3+}/[Ru(bipy)_3]^{2+}$
and
Iron(III)/Iron(II),

or, as a last example, in the iodine-iron system there are:

I_3^-/I^-
and
Iron(III)/Iron(II).

Depending on the composition of the system, these redox couples are accompanied by several equilibria which may have great influence on the reactivity.

An important entity for discussing redox systems is the reduction degree which we call r. It is a measure for the number of redox equivalents which are donated to a system relative to a well defined starting position. The reduction degree characterizes this system, whether or not it performs a photoredox reaction under illumination. The reduction degree r has been introduced to discuss redox systems of the type[8,9]:

quinone (Q) + hydroquinone (H) $\rightleftharpoons$ 2 semiquinone (S)

$$r = \frac{[S] + 2[H]}{2\cdot\{[Q] + [H] + [S]\}}\ ; \quad 0 < r < 1 \qquad (1)$$

We have found that the reduction degree - defined in a more general way than in equation (1) - can be used as an important degree of freedom not only to understand systems at equilibrium but also to describe photoredox systems far from equilibrium[3,10,11].

As an example I will treat the iron-thionine system in 0.1 molar sulfuric acid, containing a complexing agent X. In 0.1 molar sulfuric acid the concentrations of iron hydroxides are very small and the thionine is protonated. At least the following equilibria have to be considered:

$$TH^+ + Fe^{2+} \rightleftharpoons TH_2^+ + Fe^{3+} \qquad K_1(pH=1) = 4\cdot10^{-7}\ a) \qquad (2.1)$$

$$TH^+ + TH_2 + H^+ \rightleftharpoons 2TH_2^+ \qquad K_2(pH=1) = 4.3\cdot10^{-3}\ a) \qquad (2.2)$$

$$Fe^{2+} + SO_4^{2+} \rightleftharpoons FeSO_4 \qquad K_3 = 30\ 1/Mol\ b) \qquad (2.3)$$

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+ \qquad K_4 = 204\ 1/Mol\ c) \qquad (2.4)$$

$$Fe^{2+} + X \rightleftharpoons Fe(II)X \qquad K_5 \text{ arbitrary} \qquad (2.5)$$

$$Fe^{3+} + X \rightleftharpoons Fe(III)X \qquad K_6 \text{ arbitrary} \qquad (2.6)$$

a) ref. 12
b) estimated value
c) ref. 13

Concentrations of eleven species have to be calculated from six equilibria. This means that we need five conditions for a complete description. Using the abbreviations G_i for the total amount of independent species and r for the reduction degree, the five conditions can be written in the following way:

$$G_1 = TH^+ + TH_2^+ + TH_2 \qquad (3.1)$$

$$G_2 = Fe^{2+} + FeSO_4 + Fe(II)X + Fe^{3+} + FeSO_4^+ + Fe(III)X \qquad (3.2)$$

$$G_3 = Fe(SO_4) + FeSO_4^+ + SO_4^{2-} \qquad (3.3)$$

$$G_4 = Fe(II)X + Fe(III)X + X \qquad (3.4)$$

$$r = \frac{(TH^+ + 2TH_2) + (Fe^{2+} + FeSO_4 + Fe(II)X)}{2G_1 + G_2}$$

The G_i values are used as parameters and the reduction degree r is the variable. r is written according to the definition given in[10]. For discussing the stationary state, it is useful to introduce the partial reduction degrees r_1 and r_2 [11]:

$$r_1 = \frac{[TH]^+ + 2[TH_2]}{2G_1} \qquad (4.1)$$

$$r_2 = \frac{[Fe^{2+}] + [FeSO_4] + [Fe(II)X]}{G_2} \qquad (4.2)$$

With the abbreviation $v_2 = G_2/G_1$ the connection between r and r_1, r_2 is given by

$$r = (2r_1 + v_2 r_2)/(2 + v_2) \qquad (4.3)$$

If a sample is irradiated at a chosen reduction degree r_0 the photoredox reaction as given by equation (5) takes place[5]. The individual concentrations are shifted from their equilibrium values

$$TH^+ + Fe^{2+} \xrightarrow{\text{illum.}} TH_2^+ + Fe^{3+} \qquad (5)$$

The value of $r = r_0$ remains unchanged. Since no reduction equivalents are supplied to the system during illumination, r is an invariant under illumination. But of course, r_1 and r_2 change. In the left part of Figure 1 the normalized equilibrium concentrations of the reaction partners (2.1) to (2.6) are shown. The parameters $G_1 = 5 \cdot 10^{-4}$ Mol/lt, $v_2 = 8$, $v_3 = G_3/G_1 = 100$ and $v_4 = G_4/G_1 = 1$, $K_5 = 1$, $K_6 = 1$ have been used. No significant complexation with the ligand X can take place under these conditions. The concentrations of the eleven species have been calculated according to a method described earlier[14], which is discussed in the appendix. The total height of the figure corresponds to the total concentrations G_1, G_2 respectively. In this context the change of the concentrations of X and SO_4^{2-} is not of interest. Therefore, they are not drawn. For the equilibrium redox potential

$$E_{TH^+/TH_2^+} = E_{Fe^{3+}/Fe^{2+}} = E^\circ_{Fe^{3+}/Fe^{2+}} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad (6)$$

the total height of the figure is equal to 1 Volt. It is interesting that the main iron species are the sulfato complexes $Fe(SO_4)^+$ and $FeSO_4$, a fact which sometimes seems to be overlooked in the literature. In contrast to the iodine/iron system[10] there is a sharp change of the concentrations as soon as the iron is completely reduced. This means that r_1 and r_2 in eq. (4.1) and (4.2) are nearly independent.

It would be very interesting to know the change of concentration of the eleven different species in steady state conditions. To calculate the concentrations in the photostationary state we assume that in this state all reactions except (2.1) are at equilibrium. The variable to choose is the partial reduction degree r_1 as defined by eq. (4.1). To carry out the calculations we take the equilibrium concentrations at the deliberately chosen reduction degree r_0 as starting point. The redox equilibrium (2.1) is disturbed as a consequence of the photoreaction (5). Therefore, it has to be replaced in the calculation by another condition. Since r_1 is the variable, the new condition is given by eq. (4.1). Details of the calculation are shown in the appendix. After having derived the non-equilibrium concentrations at the reduction degree r_0, it is possible to calculate the half cell potentials $E_{Fe^{3+}/Fe^{2+}}$ and E_{TH^+/TH_2^+} as

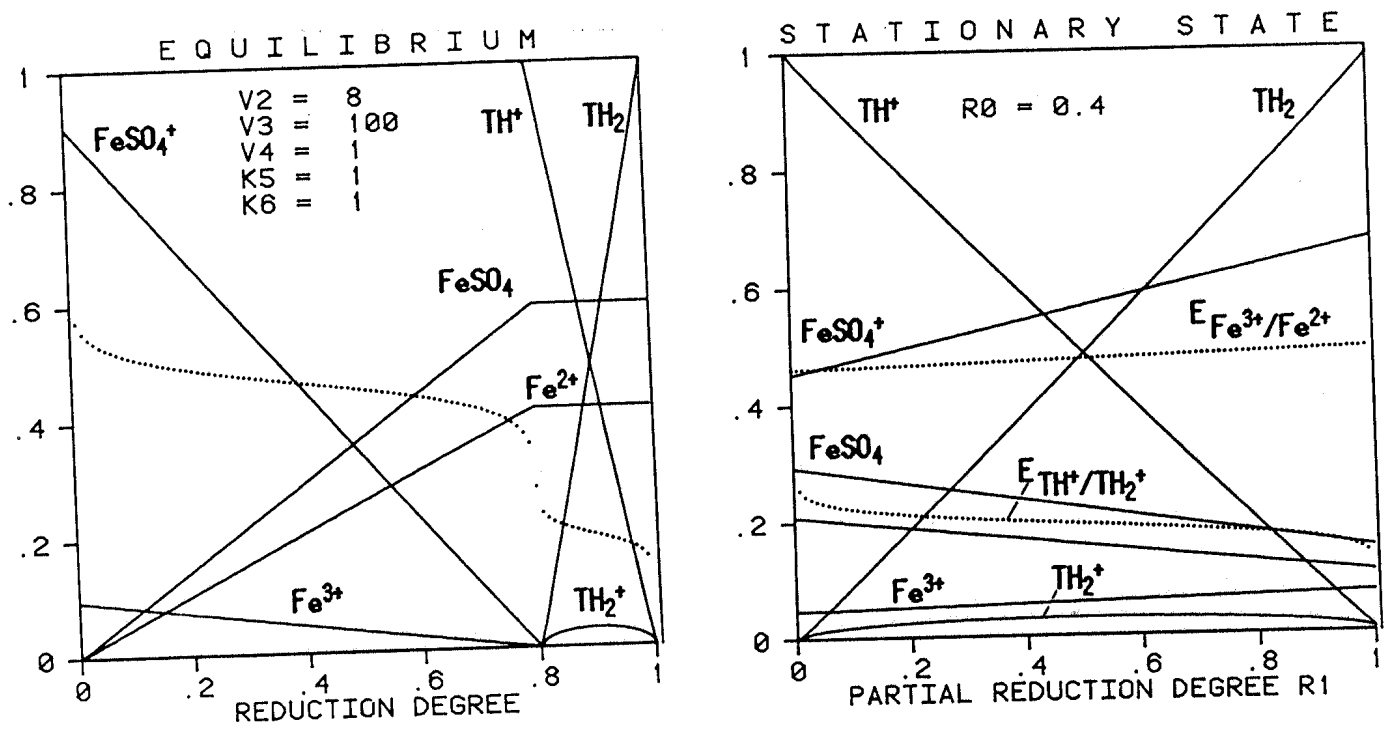


Fig. 1: EQUILIBRIUM: normalized equilibrium concentrations versus the reduction degree. The dotted line corresponds to the equilibrium redox potential, eq. (6).
STATIONARY STATE: normalized nonequilibrium concentrations versus the partial degree r_1, eq. (4.1), for the reduction degree $r = r_0 = 0.4$. The dotted lines show the half cell potentials. The total height of the picture corresponds to 1 Volt.

follows:

$$E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad (7.1)$$

$$E_{TH^+/TH_2^+} = E^{\circ}_{TH^+/TH_2^+} + \frac{RT}{F} \ln \frac{[TH^+]}{[TH_2^+]} \qquad (7.2)$$

The calculated photostationary concentrations and the half cell potentials are shown in the right part of Figure 1. Since the total iron(II) concentration at $r_1 \approx 0$ is 4 times larger than $[TH^+]$, $E_{Fe^{3+}/Fe^{2+}}(r_1)$ remains nearly constant in the whole interval $0 < r_1 < 1$ and is approximately equal to the equilibrium potential. This corresponds to a practical situation because it is necessary to choose the concentration of iron(II) significantly larger than that of $[TH^+]$ to get high quantum efficiency for reaction (5) [5]. There is a sudden change of the thionine potential E_{TH^+/TH_2^+} right at the beginning. This sudden change corresponds to the potential jump at $r = 0.8$ in the equilibrium situation. The exchange current density for iron(III)/iron(II) on platinum[15] or gold electrodes in sulfuric acid is small compared to the exchange current density of the thionine couple. This is even more pronounced when applying coated platinum electrodes[16]. Therefore, if two platinum or gold electrodes are immersed in an iron-thionine solution and one of these electrodes is irradiated and the other one is kept in the dark, nearly the total potential difference

$$E_{Fe^{3+}/Fe^{2+}}(r_1) - E_{TH^+/TH_2^+}(r_1) \approx E_{dark} - E_{illuminated}$$

can be observed. Another method consists in applying a doped tin dioxide electrode for the iron(III)/iron(II) couple and a gold or platinum electrode for the thionine[5,11].

The achieved efficiency of the iron-thionine systems is much lower than what could be expected from the absorption region and the photostationary state calculations. The efficiency of the best systems has been reported to be less than 0.05% [17]. We know the reasons. The most important one is the very low current collection efficiency*) due to the fast recombination

$$\text{Iron(III)} + \text{reduced thionine} \longrightarrow \text{Iron(II)} + TH^+ \qquad (8)$$

*) The current collection efficiency is defined as the flux of electrons flowing in the limiting photocurrent at the illuminated electrode divided by the incident flux of photons.

Brooken-Zijp et al. have published that the addition of fluorine ions which form very stable complexes with iron(III) increase the cell efficiency significantly[18], because the velocity of reaction (8) is slowed down. However, complexation of iron(III) decreases the achievable open circuit voltage in the whole range $0 < r_1 < 1$. This is shown in Figure 2. Therefore, complexation of iron(III) cannot really be used to solve the problems inherent to the iron-thionine system. However, much larger open circuit voltages can in principle be achieved if iron(II) but not iron(III) is stabilized by complexation; see Figure 3. The nonequilibrium concentrations in Figures 2 and 3 have been calculated at the same reduction degree $r_0 = 0.4$ as in Figure 1.

We have to conclude that for solar energy conversion only conditions as shown in Figure 3 can be the basis for further investigations on the iron-thionine and similar systems, because thermodynamics can never be violated. Up to now no ideas have been published as to how such a situation could be achieved in a homogeneous reaction. Albery et al. have shown that the collection efficiency can be expressed in terms of characteristic lengths[19]. From these arguments we feel that it will not be possible to design an efficient photogalvanic cell with systems that follow the Rehm-Weller[20] or Agmon-Levin[21] behaviour in the recombination reaction.

$$\Delta G^{\#} = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2}\right)^2 + (\Delta G^{\#}(0))^2\right]^{1/2} \quad ; \text{ Rehm and Weller} \qquad (8.1)$$

$$\Delta G^{\#} = \Delta G + \frac{\Delta G^{\#}(0)}{\ln 2} \cdot \ln\left\{1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^{\#}(0)}\right)\right\} \quad ; \text{ Agmon and Levin} \qquad (8.2)$$

ΔG is the free enthalpy difference and $\Delta G^{\#}(0)$ is the free energy of activation for a reaction with $\Delta G = 0$ and can be calculated from the barrier of the self exchange of the two reaction partners: $\Delta G^{\#}(0) = (\Delta G_A^{\#} + \Delta G_D^{\#})/2$. We should not forget that these free energy relations and also the advanced quantum mechanical treatments[22] describe a one electron exchange which may include vibrations but not significant nuclear rearrangements. Fortunately one can observe photoredox reactions for which these theoretical pictures are not sufficiently complete. I will report on two such systems which have been studied in our laboratory. The first is the iron-iodine reaction on which details have been published recently[3]. The second ones are the silver halide zeolites where new observations have been made.

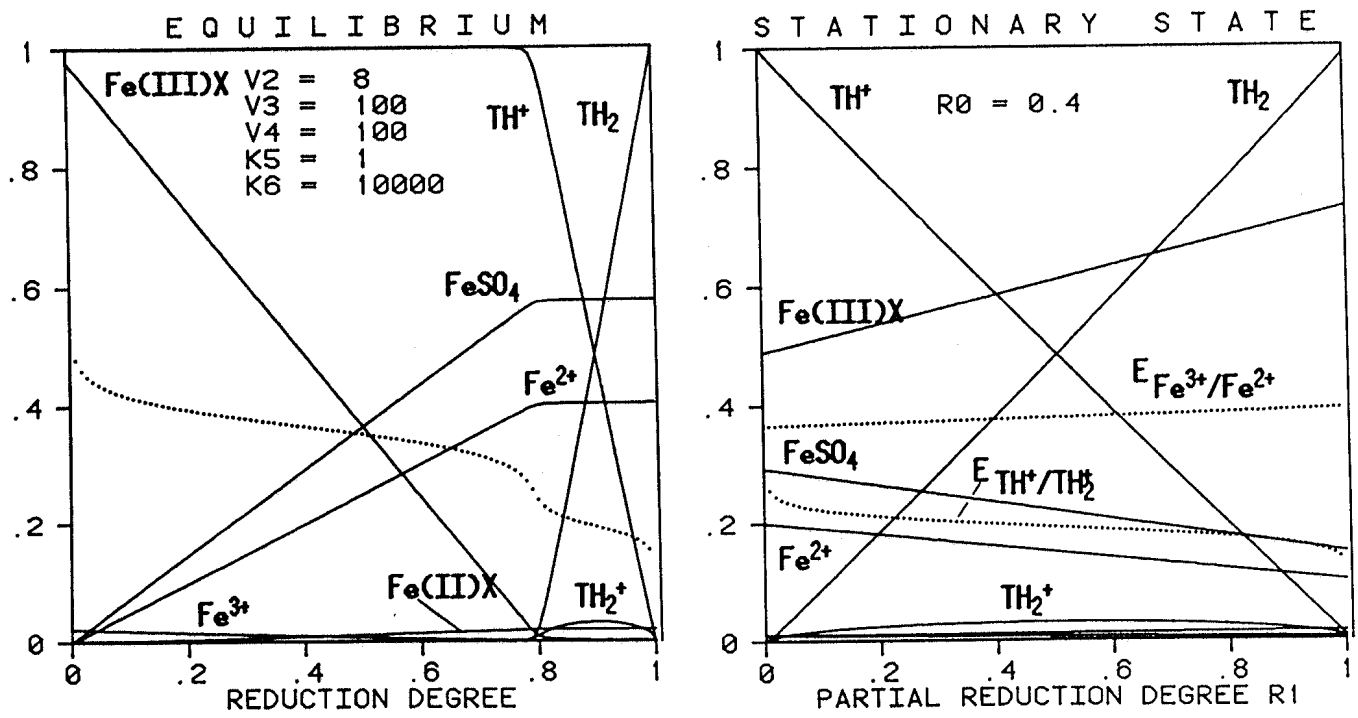


Fig. 2: The same as in Figure 1, but for different values of K_6 and v_4.

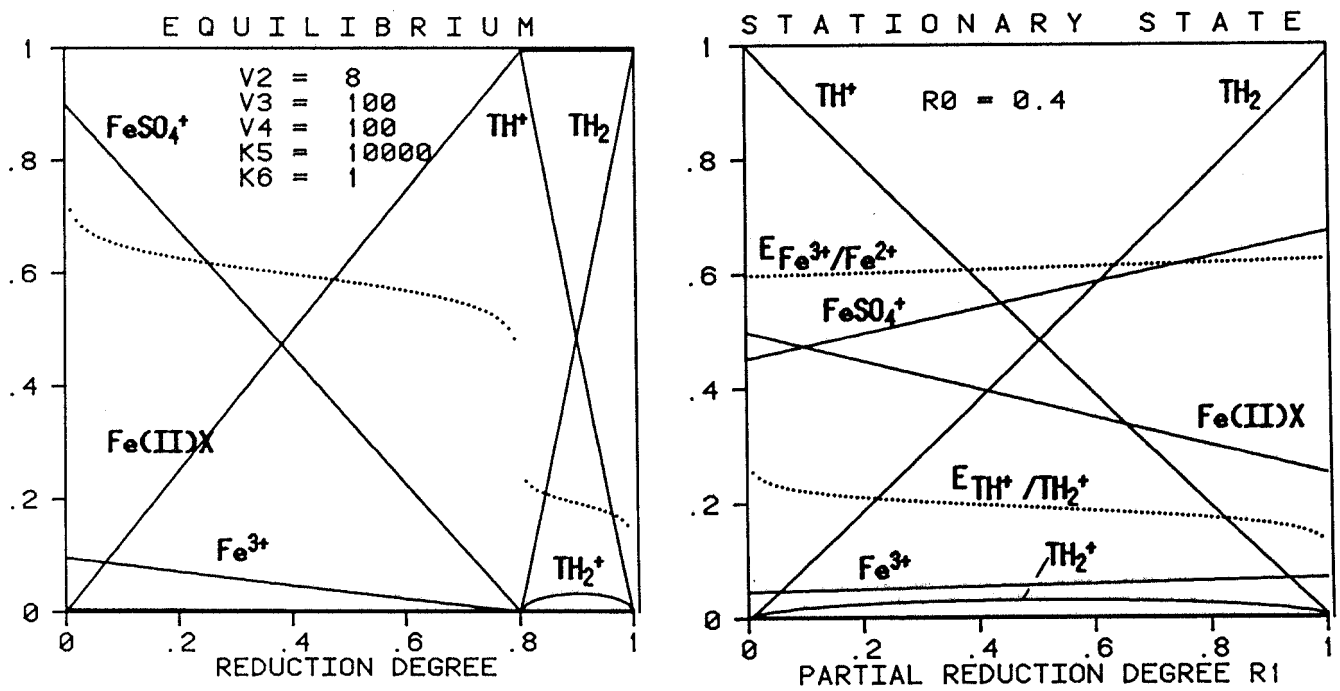


Fig. 3: The same as in Figure 1, but for different values of K_6 and v_4.

III. The Iron-Iodine Photoredox System[3]

For more than 50 years it has been known that the equilibrium

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^- \qquad (9)$$

can be shifted to the left by irradiation with visible light. Electrons are transferred from iron(II) species to energetically excited iodine species:

$$(I_2 \text{ or } I_3^-) \xrightarrow{\text{visible light}} (I_2 \text{ or } I_3^-)^* \qquad (10.1)$$

$$(I_2 \text{ or } I_3^-)^* + 2Fe^{2+} \longrightarrow (2I^- \text{ resp. } 3I^-) + 2Fe^{3+} \qquad (10.2)$$

This reaction has been considered for solar energy utilization[24]. We have, therefore, made detailed experimental and theoretical investigations. Our experiments have been carried out in 0.1 molar sulfuric acid, in which the concentrations of $Fe(OH)^{2+}$ and $Fe_2(OH)_2^{4+}$ are very small. The equilibria to be considered at 25°C are[3]:

$$2Fe^{3+} + 3I^- \rightleftarrows 2Fe^{2+} + I_3^- \qquad K_1 = 9.94 \cdot 10^7 \ (1/\text{Mol})^2 \qquad (11.1)$$

$$I_2 + I^- \rightleftarrows I_3^- \qquad K_2 = 714.3 \ 1/\text{Mol} \qquad (11.2)$$

$$I_2(\text{solid}) \rightleftarrows I_2(\text{solved}) \qquad K_3 = 1.34 \cdot 10^{-3} \ \text{Mol/l} \qquad (11.3)$$

$$Fe^{3+} + I^- \rightleftarrows FeI^{2+} \qquad K_4 = 708 \ 1/\text{Mol} \qquad (11.4)$$

$$Fe^{3+} + SO_4^{2-} \rightleftarrows FeSO_4^+ \qquad K_5 = 204 \ 1/\text{Mol} \qquad (11.5)$$

$$Fe^{2+} + SO_4^{2-} \rightleftarrows FeSO_4 \qquad K_6 = 30 \ 1/\text{Mol} \qquad (11.6)$$

As mentioned before, we have succeeded in finding a general definition for the reduction degree . Its application to the present system which is in general not homogeneous due to (11.3) leads to:

$$r = \frac{\{[I^-] + [I_3^-] + [FeI^{2+}] + 2[FeI_2^+]\} + \{[Fe^{2+}] + [FeSO_4]\}}{I_{tot} + M_0} \qquad (12.1)$$

I_{tot} is equal to the total iodine concentration:

$$I_{tot} = [I^-] + 2[I_2(\text{solved})] + 3[I_3^-] + [FeI^{2+}] + 2[FeI_2^+] + 2I_2(\text{solid}) \cdot \frac{1}{V} \qquad (12.2)$$

The symbol V is used for the volume. The total concentration on solved iodine species is called I_0:

$$I_0(r) = [I^-] + 2[I_2(\text{solved})] + 3[I_3^-] + [FeI^{2+}] + 2[FeI_2^+] \qquad (12.3)$$

At equilibrium I_0 depends on the reduction degree only if $I_0 < I_{tot}$. M_0 is equal to the total concentration of iron ions. The forth condition we need in order to calculate the concentrations of the ten species as a function of the reduction degree is the sulfate concentration S_0:

$$S_0 = [SO_4^{2-}] + [FeSO_4^+] + [FeSO_4] \qquad (12.4)$$

Figure 4 gives the normalized equilibrium concentrations of the reaction partners (11.1) to (11.6) for the parameters $M_0 = 0.02$ mol/l, $I_0 = 0.02$ mol/l and $S_0 = 0.1$ mol/l. As in the Figures 1 to 3, the total height of the picture corresponds to the concentrations I_{tot}, M_0 respectively. For the redox potential it is equal to 1 Volt.

As discussed in Chapter II, it is very interesting to calculate the change of concentration for the different species under illumination. An important difference between the iron-thionine system and the iron-iodine system is that the thermal back reaction

$$2Fe^{3+} + 3I^- \longrightarrow 2Fe^{2+} + I_3^- \qquad (13)$$

is very slow. Photostationary state conditions can therefore be applied.

As in the previous example, we take the equilibrium concentrations at the chosen reduction degree $r = r_0$ as starting point for the calculation. The redox equilibrium (11.1) is disturbed as a consequence of the photoinduced reaction. We could use the partial reduction degree as before. Another possibility is to apply the decrease of iron(II) species as expressed by the following equation:

$$\%[\Delta Fe^{2+}] = \left| \frac{\Delta[Fe^{2+}] + \Delta[FeSO_4]}{[Fe^{2+}]_{eq} + [FeSO_4]_{eq}} \right| \cdot 100 \qquad (14)$$

$[Fe^{2+}]_{eq}$ and $[FeSO_4]_{eq}$ are the equilibrium concentrations of these two species. If $2\{[I_2]_{eq} + [I_3^-]_{eq}\}$ is smaller than $\{[Fe^{2+}]_{eq} + [FeSO_4]_{eq}\}$, it is not possible to oxidize all iron(II) to iron(III). After having derived the nonequilibrium concentrations at the reduction degree $r = r_0$, it is possible to calculate the half cell potentials as follows:

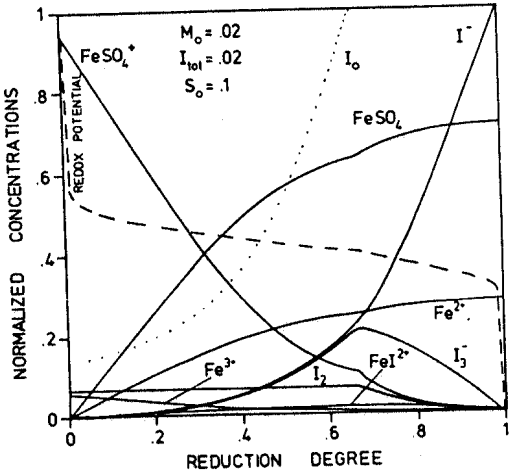
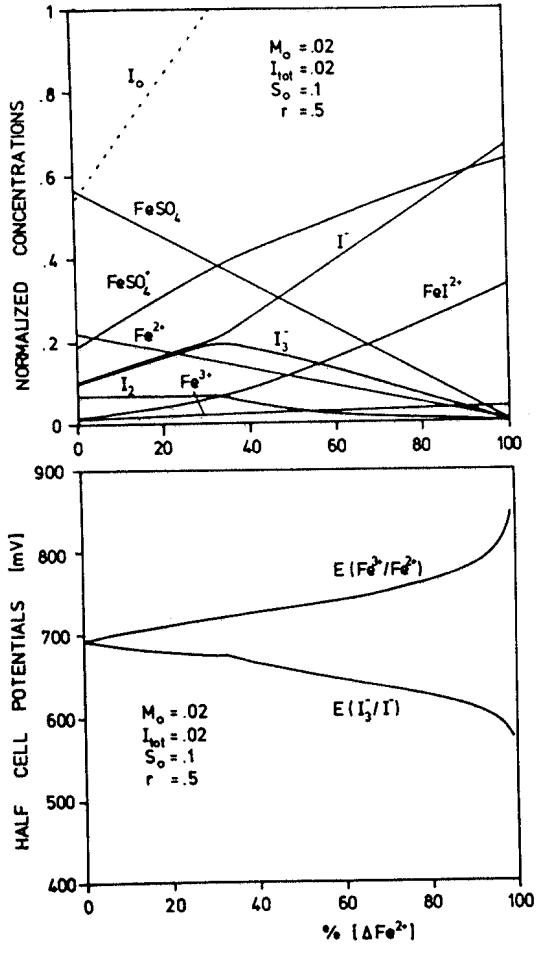


Fig. 4: EQUILIBRIUM: Normalized equilibrium concentrations and equilibrium redox potential versus the reduction degree. The dottet line corresponds to the total concentration $I_0(r)$ of solved iodine species.
PHOTOSTATIONARY STATE: Normalized concentrations and halv cell potentials versus $\%[\Delta Fe^{2+}]$ for r = 0.5. At the starting point $\%[\Delta Fe^{2+}] = 0$ the concentrations and potentials correspond to the equilibrium situation r = 0.5.



$$E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad (15.1)$$

$$E_{I_3^-/I^-} = E^{\circ}_{I_3^-/I^-} + \frac{RT}{2F} \ln \frac{[I_3^-]}{[I^-]^3} \qquad (15.2)$$

$E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77$ V

$E^{\circ}_{I_3^-/I^-} = 0.534$ V

The results are shown in Figure 4. The behaviour of the iron-iodine system is more complicated than that of the iron-thionine system. We have found that both the quantum efficiency of the reaction (10.2) and the half cell potential as a function of $\%[\Delta Fe^{2+}]$ depend strongly on the initial conditions[3]. It has been possible to build a flow system in which both electrodes are kept in the dark because of the slow back reaction which takes hours or even days and because of the existence of selective electrodes. The selective electrodes are glassy carbon for the I_3^-/I^- and doped tin dioxide for the Fe^{3+}/Fe^{2+} couple. The following parameters have been measured: light intensity at given spectral distribution, potential of the two selective electrodes versus a reference electrode, light absorption of the solution at constant wave length, temperature at the electrode surface and electrical current between the two selective electrodes at variable external resistance. Our experimental set-up is shown in Figure 5, and two typical experimental curves are shown in Figure 6. Irradiation starts at the points "start" and stops at the points "stop". The upper curves demonstrate the change of light absorption at 490 nm. The lower curves visualize the change of potential of each selective electrode compared to normal hydrogen electrodes. $E_{Fe^{3+}/Fe^{2+}}$ is observed on doped and sintered tin dioxide and $E_{I_3^-/I^-}$ on glassy carbon. At the point "current" different external resistances R_L have been applied; see Fig. 5. The solution in case B is oversaturated. The extinction at the beginning of the experiment has therefore not been constant; see ref. 3.

The observed short circuit potential is not equal to the equilibrium potential. This is due to polarization phenomena[25] which have not yet been studied in relation to this system. The light absorption is not influenced by the current. This means that even at short circuit conditions the concentrations of the photochemically produced species in our system are not influenced by the electrical current flow. This is because the electrode surface of 1.5 cm^2 is very small compared to the volume. Theoretical results as shown in Figure 4 enable a comparison between the calculated half cell

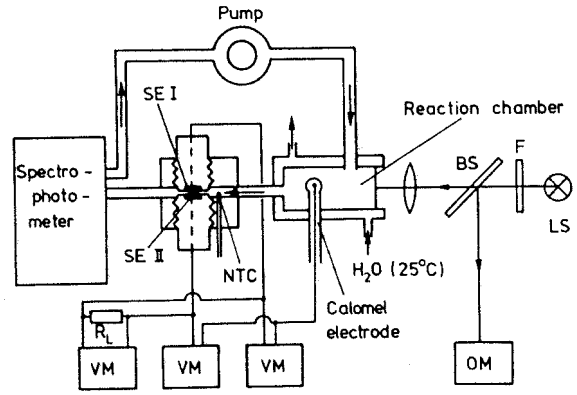


Fig. 5: Experimental set-up for the observation of photogalvan behaviour of the iodine/iron system. LS = light source, 200 wat HBO W/2 Osram, BS = beam splitter. OM = calibrated optometer; 80 United Detector Technology Inc. VM = voltmeter. R_L external res tor. SE I and SE II = selective electrodes (SE I = glassy carbon SE II = sintered and doped tin dioxide). F = filter.

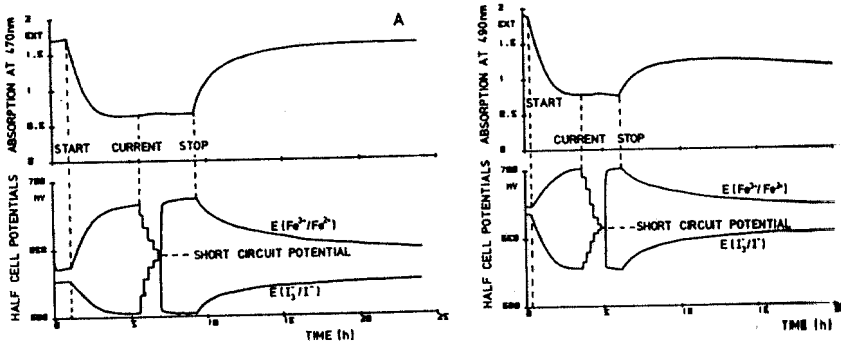


Fig. 6: Observed light absorption and half cell potentials ve time for two different solutions; see ref. 3.

potentials and the observed ones. Quantitative agreement cannot be expected since the activity coefficients have not been considered and since the selectivity of the electrodes is perhaps not 100%. Nevertheless at least qualitative agreement between calculated and measured curves should be observed. Results as shown in Figure 7 demonstrate that this is the case.

The iron-iodine system is complicated. But using the reduction degree as important degree of freedom we have succeeded in deriving at least a reasonable phenomenological description which can guide us to make experiments and to interpret them. From our results we have estimated that up to 0.3% solar energy can be transformed into electrical energy. This seems to be the upper limit so that even this nice system can no more be of interest for solar energy conversion, if no way can be found to make the difference between the half cell potentials much larger. From a theoretical point of view there exists a similar possibility as described for the iron-thionine system. This is stabilization of the iron(II); see ref. 3. A different way is to use another redox couple than iron(III)/iron(II) with significantly larger normal potential $E^{\circ}_{Ox/Red} >> E^{\circ}_{Fe^{3+}/Fe^{2+}}$. It is not known whether such a situation can be realized. But when we tried to improve this system, we have observed very interesting photopotentials with a chromium-iodine solution.

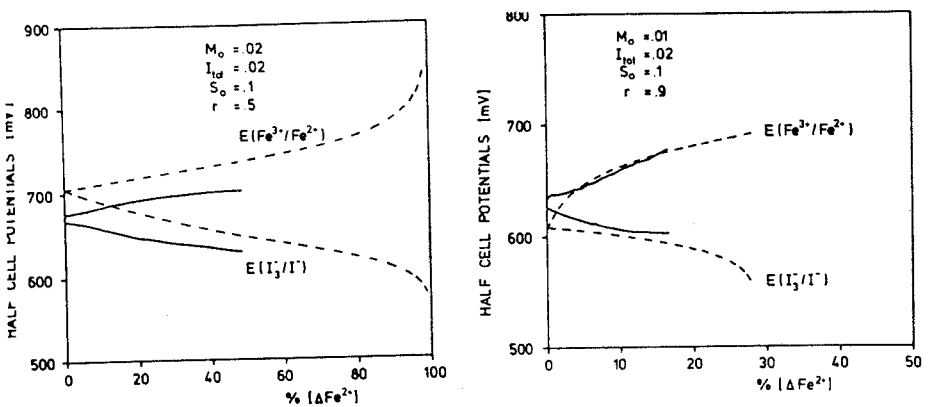


Fig. 7: Comparison between the calculated (---) and the measured (——) half cell potentials for two different solutions, see ref. 3.

IV. Photochlorine Evolution in Silver Zeolites

More than one year ago[4] we have observed that a silver electrode which is immersed in an aqueous sodium chloride solution containing chlorine, remains at the Ag/AgCl potential, while a graphite or platinum electrode takes immediately the Cl_2/Cl^- potential. If a resistor is put between the silver and the platinum electrodes, the observed current is limited by the transport of Cl_2 to the platinum electrode. The Ag/AgCl potential remains nearly constant even with significant current densities. It is interesting that the oxidation of silver by Cl_2 is slow, despite of the large driving force. The conclusion from these experiments is that the barrier for the following overall reactions is high[28].

Electrode reaction:

$$e + [nAg,mAgCl] + \frac{1}{2}\,Cl_2 \xrightarrow{\text{very slow}} [nAg,mAgCl] + Cl^- \qquad (16.1)$$

Oxidation of silver:

$$[nAg,mAgCl] + \frac{1}{2}\,Cl_2 \xrightarrow{\text{slow}} [(n-1)Ag,(m+1)AgCl] \qquad (16.2)$$

But of course the reaction

$$[nAg,mAgCl] \pm e \xrightarrow{\text{very fast}} [(n\pm1)Ag,(m\mp1)AgCl] \pm Cl^- \qquad (16.3)$$

is fast as we know from the high reversibility of silver/silverchloride electrodes. This behaviour explains some of the interesting observations which are described below.

It has long been known that aqueous ~~suspensions~~ dispersions of silver salts produce oxygen on illumination[26]. Similar behaviour has been observed a few years ago on silver ion exchanged zeolites[27]. One of the advantages of zeolite systems is that stable suspensions can be obtained very easily.

$$[Ag^+]_n[Zeol] + mH_2O \xrightarrow[>350\ nm]{h\nu} [Ag_n]^{(n-r)+}[Zeol] + (m-r/2)H_2O + rH^+ + r/4\ O_2 \qquad (17)$$

We have observed interesting pH dependences of photooxygen evolution by means of an accurate but simple method[28] developed in our laboratory[29].

Recently we have found that in presence of Cl^- or Br^-, silver zeolite suspensions in water do not produce oxygen under irradiation at wavelengths $\lambda \geq 350$ nm within a broad pH range. Chlorine and bromine are the photoproducts instead of oxygen[4,28].

$$[Ag^+]_n[Zeol](mCl^-)_{ads} \xrightarrow[>350\ nm]{h\nu} [Ag_n]^{(n-r)+}[Zeol]((m-r)Cl^-)_{ads} + r/2\ Cl_2 \qquad (18)$$

Comments on the photoproduction of halogens from silver halides have appeared in the literature[26,30-32]. But in general this reaction which leads to a good storage capacity - $Ag,AgCl|HCl(1m)|Cl^-$, $1/2\ Cl_2$, $\Delta E° = 1.14$ Volt - has been ignored. The reason why reaction (18) is very interesting, is the slow back reaction (16.2). It is, therefore, easy to separate the photoproducts, e.g. by filtration or by using the solubility of chlorine and bromine in graphite[33]. This means that energy storage can be achieved. If a silver electrode and a graphite or platinum electrode are immersed in a silver-zeolite suspension containing Cl^-, a potential difference between the silver electrode and the graphite or platinum electrode of about 1 Volt is observed a few minutes after illumination. As mentioned above, the silver electrode remains at the Ag/AgCl potential while the counter electrode adopts the Cl_2/Cl^- potential. As soon as enough chlorine has been produced, currents of more than 0.1 mA/cm^2 at up to 700 mV cell voltage have been observed in our experimental arrangement which is shown schematically in Figure 8.

There are a few problems related to this, however. We would like to use this system for energy storage. But in practical applications the photoproduced silver can only appear as photocatalyst and not as storage material. - The system has to be sensitized. Unfortunately, organic sensitizers are useless since they are not stable against chlorine or bromine. - It is also important not to forget that zeolites, depending on their composition, are only stable within certain experimental conditions.

During our studies regarding the reoxydation of the photochemically produced silver we have observed the catalytic reaction reported in Figure 9. Sodium zeolite A [34] was exchanged to 97% by Ag^+. 0.25 g of this zeolite was introduced into the photoreactor[29] and pH 4 was established by adding 0.1 molar sulfuric acid. The suspension was irradiated through a pyrex filter during 4 hours with a 200 Watt high pressure mercury lamp. Now KCl was added to obtain a 0.2 mKCl solution. Portions of a $2 \cdot 10^{-3}$ molar Cl_2 solution were added and the potential of a platinum electrode versus a calomel electrode was measured.

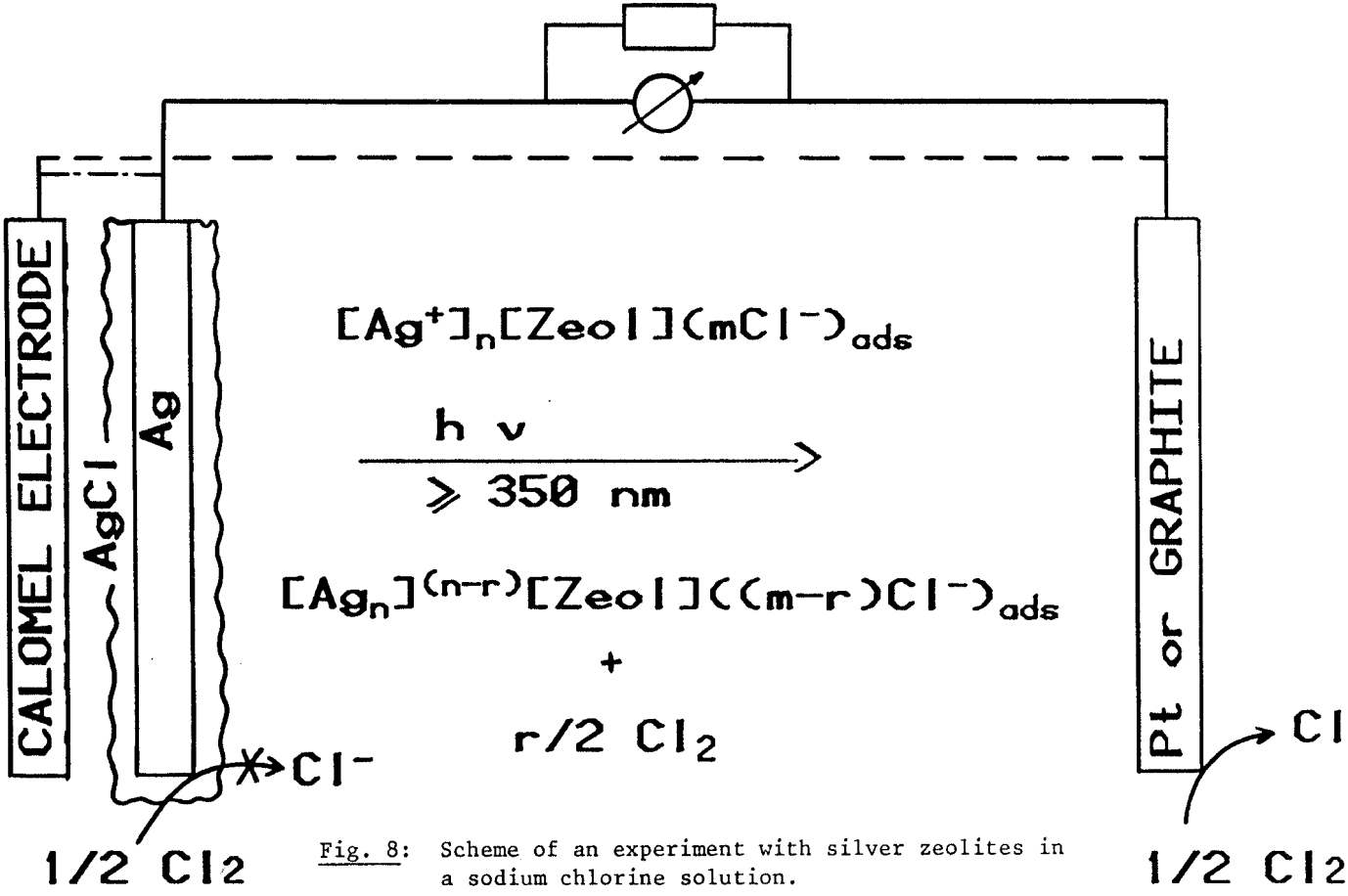


Fig. 8: Scheme of an experiment with silver zeolites in a sodium chlorine solution.

As shown in Figure 9 the potential of the platinum electrode increased immediately after addition of Cl_2 and decreased slowly within some minutes due to the oxydation of Ag. This experiment was repeated after addition of a portion of 90 mg $CuCl_2$ and then no fast increase of the potential could be observed. This means that the added Cl_2 was immediately reduced by the silver. The explanation of this fact is that Cu^{2+} acts as catalyst for the oxidation of silver by chlorine, probably due to the formation of Cu^+ as we shall see below.

$$[Ag_n]^{(n-r)}[Zeol] + \frac{1}{2}\,Cl_2 \xrightarrow[\text{catalyst}]{Cu^{2+}\text{ as}} [Ag_{n-1}]^{(n-1-r)}[AgCl][Zeol] \qquad (19)$$

But even with addition of Cu^{2+}, only part of the silver can be oxydized by the Cl_2 under these conditions. This is shown by the rise of the potential after each addition of Cl_2. Under appropriate conditions it should be possible to reduce Cu^{2+} to Cu^+ with the photochemically reduced silver zeolite, if the formation of Cu^+ is responsible for the catalytic reaction. It has long been known that in presence of Cl^- and above 160°C, the following reaction takes place as a consequence of the low solubility of AgCl [35] and CuCl.

$$Ag + CuCl_2 \longrightarrow AgCl + CuCl \qquad (20)$$

As an example a foil of Ag of 0.02 mm thickness is oxydized completely at 160°C to a foil of AgCl, according to equation (20) [36].

We have tried to reoxydize the photochemically produced silver with Cu^{2+} and have observed the following reaction:

$$[Ag_n]^{(n-r)}[Zeol]((m-r)Cl^-)_{ads} + u[Cu^{2+}] \xrightarrow[\text{ammoniacal solution, pH 9.5, 25°C}]{Cl^-\text{ solution with } Cu^{2+},\ 160°C} [Ag_n]^{(n-r+u)}[Zeol]((m-r+u)Cl^-)_{ads} + u[Cu^+] \qquad (21)$$

These studies are not yet complete. The conditions under which the stoichiometry becomes exactly as it should be, are not yet established. But the results are good enough to speculate that we have achieved a "storage cell" of the type shown in Figure 10. Each step is experimentally proved. Several problems remain, however. We do not yet know, how complete the stoichiometry is. Therefore, we do not know how many cycles can be achieved. The sensitization problem is not yet solved.

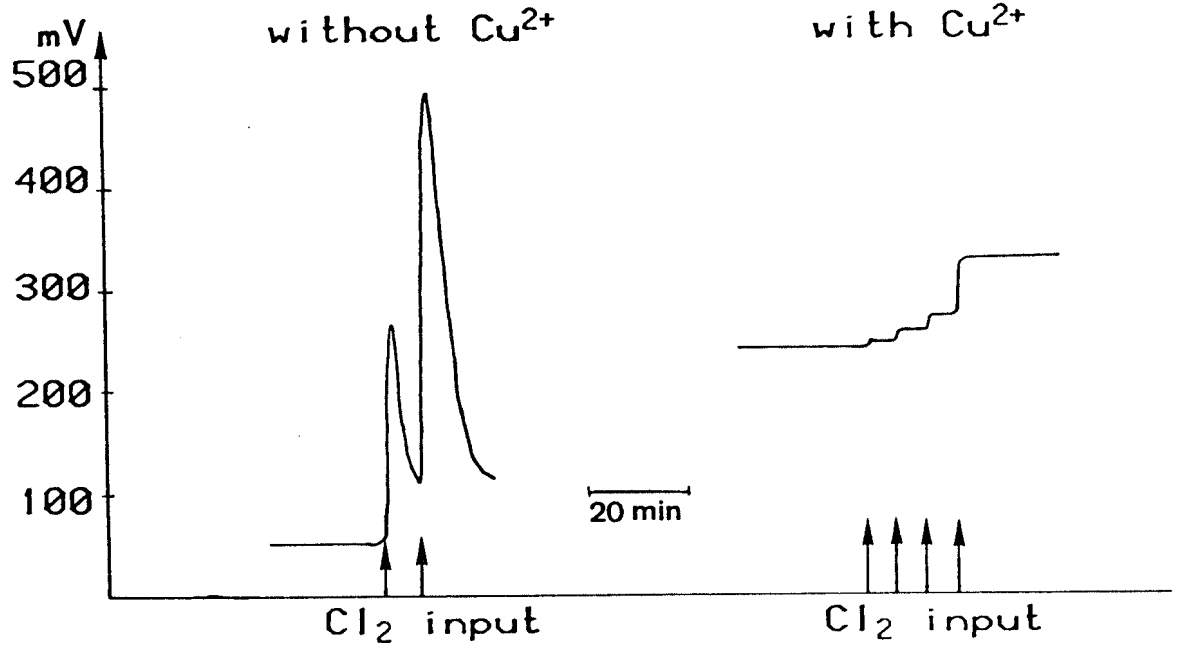


Fig. 9: Potential of a platinum electrode versus calomel in a suspension of a photoreduced silver zeolite after injection of Cl_2. The photoreduction of the silver zeolite has been made in absence of Cl^- in this experiment; reaction (17)[28].

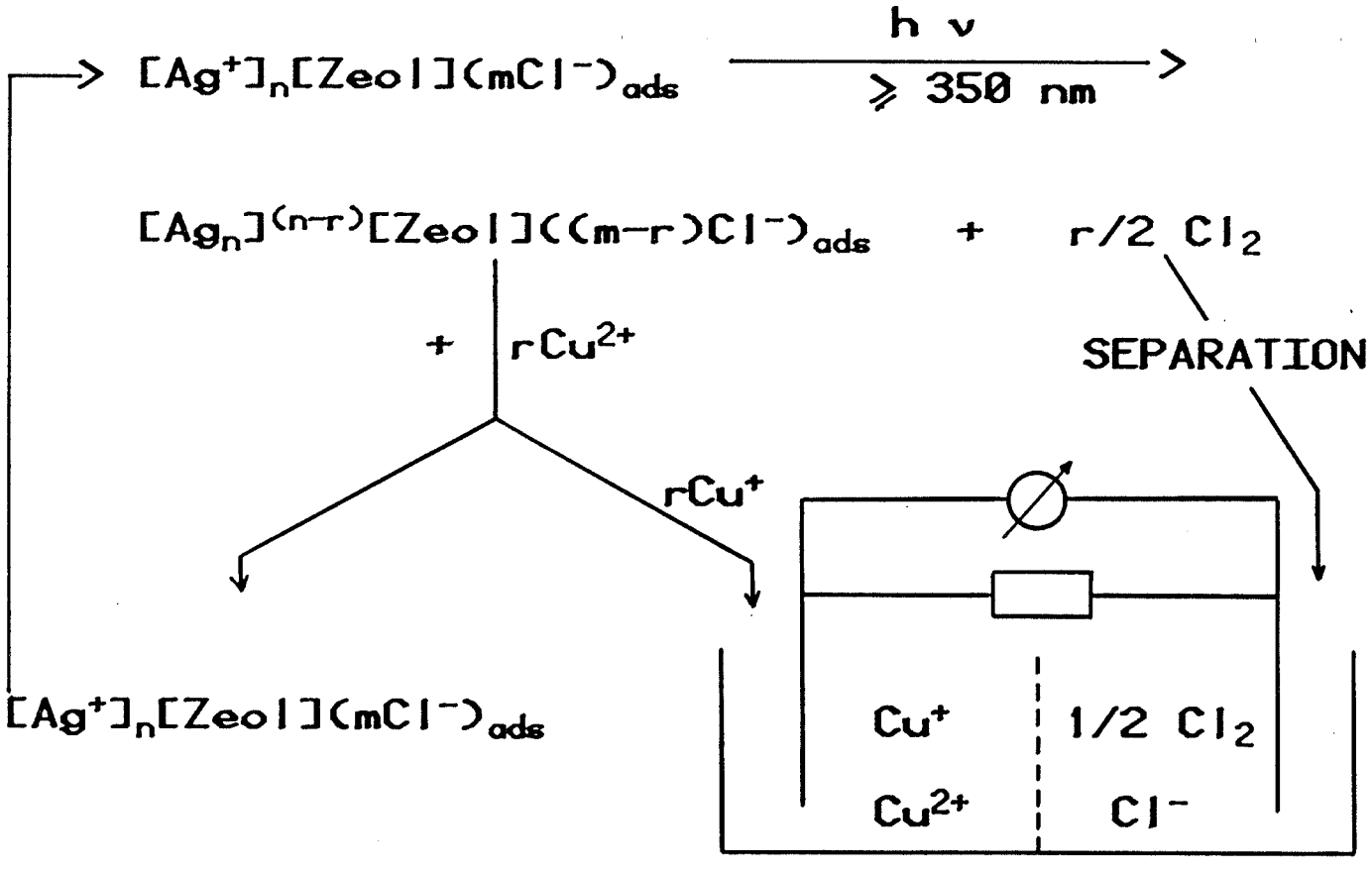


Fig. 10: Heterogeneous photogalvanic cell with energy storage.

Reoxydation with Cu^{2+} is not the only way to use the energy stored in reaction (18). From a thermodynamic point of ~~few~~ it seems possible that the photochemically produced silver clusters in reaction (17) or (18) can be used to achieve reduction of H_3O^+ to $1/2\ H_2 + H_2O$. Thermal reduction of H_3O^+ with irradiated silver zeolites has been reported twice[27]. The catalytic activity of silver on H_2 has been studied many years ago[37]. An enthalpy diagram which gives interesting information about the reduction capabilities of silver clusters is shown in Figure 11. The number in condensed phase is related to the heat of hydration of the gaseous Ag^+ ion -5.07eV [38]. The values for $(Ag_3)g$ are from Hilpert & Gingerich[39]. A similar diagram can be constructed for $\Delta G°$. It is obvious from Figure 11 that not only Ag(g) but also $Ag_2(g)$, $Ag_3(g)$ and probably much larger clusters are from a thermodynamic point of view able to reduce hydrated protons. The question is, how much energy is lost by the reaction

$$\frac{1}{n}\,(Ag_n)_g \longrightarrow \frac{1}{n}\,(Ag_n)_{env}$$

Of course, this question can only be answered relative to specific environment. Some studies regarding this question have been published[40].

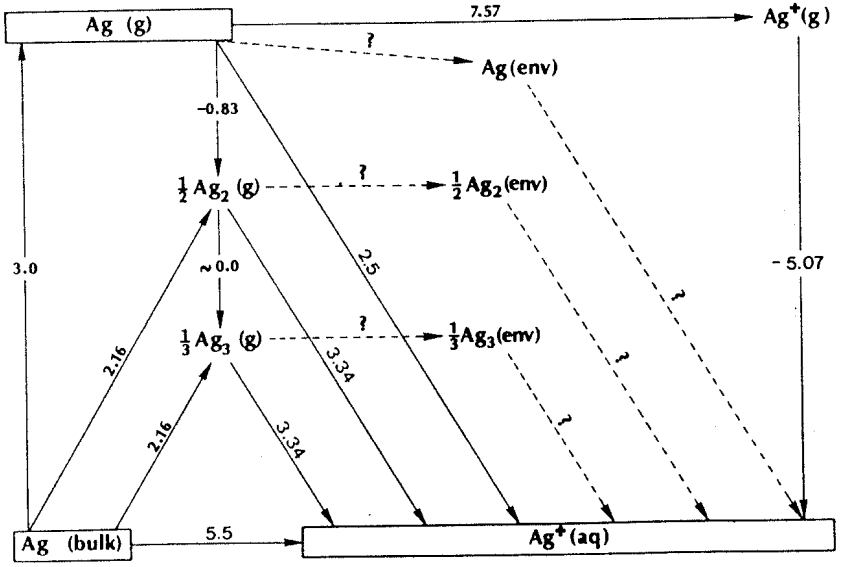


Fig. 11: Enthalpy diagram; env = environment.

V. Conclusions

In a review article of 1942 Copeland, Black and Garrett[41] have defined the photovoltaic effect as follows:

> "The photovoltaic effect is defined[42] as the production or change of potential between two electrodes separated by a suitable electrolyte or other substance when the electrodes are unsymmetrically illuminated. It is also called the 'Becquerel effect' in honour of its discoverer, Becquerel. Similar to this effect is the 'Swensson-Becquerel effect', which is the production of a photopotential upon illumination of the electrolyte only."

It is nowadays accepted by the leading people of the field[1,5,43] that systems which show the "Swensson-Becquerel effect" are identical with photoelectrochemical devices in which in a homogeneous or heterogeneous photoreaction products are formed which in a second step can react at appropriate electrodes. This means that they are identical with photogalvanic cells.

We do not know if some type of photogalvanic cells will become useful for solar energy conversion. As explained with regard to iron-thionine and iron-iodine systems, there are only specific configurations which can be excluded for practical application. Understanding why these configurations cannot be efficient will help in the development not only of photogalvanic cells but also of other possibilities for solar energy conversion. Even looking into "very old systems" can lead to surprising situations. The behaviour of silver zeolite systems in presence of Cl^- as described in part IV of this paper is an example. Another is the pH-dependence of oxygen evolution in silver zeolites in absence of halide ions[44,47]. It might be worth to reinvestigate other "old systems" as for example the reaction

$$2CuO \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} Cu_2O + \frac{1}{2}\,O_2 \qquad [45]$$

$$2CuO \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2Cu + O_2 \qquad [46]$$

and reactions of other metal oxides or metal halides. Together with new ideas[43,47-50], the field of photogalvanic cells is still open for surprising results.

Acknowledgement

This paper is part of project No. 4.340.79.04 financed by the Swiss National Science Foundation.

I should like to thank Barbara Sulzberger, Jürg Baumann, and Stephan Hug for their contributions and Professor E. Schumacher for support of this work.

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APPENDIX

Calculations of the Equilibrium Concentrations and the Concentrations in the Photostationary State

Our method to calculate equilibrium concentrations as shown in Figures 1 to 4 has been published several years ago[14]. Since then we have succeeded in finding a general definition of the reduction degree[10] which allows a phenomenological description of some properties of complex photoredox systems. Therefore, it might be helpful to describe briefly how the results shown in Figures 1 to 4 have been calculated.

By applying the abbreviations

$C_1 = [TH^+]$ $\quad C_7 = X$

$C_2 = [TH_2]$ $\quad C_8 = [SO^{2-}]$

$C_3 = [FeSO_4]$ $\quad C_9 = [TH_2^+]$

$C_4 = [FeSO_4^+]$ $\quad C_{10} = [Fe^{2+}]$

$C_5 = [Fe(II)X]$ $\quad C_{11} = [Fe^{3+}]$

$C_6 = [Fe(III)X]$

$\bar{C}_i = \log C_i$ $\quad \bar{K}_j = \log K_j$

the equilibrium conditions can be written in the following way:

$$C_1 + C_{10} \rightleftharpoons C_9 + C_{11} \qquad K_1 \qquad (A1.1)$$

$$C_1 + C_2 \rightleftharpoons 2C_9 \qquad K_2 \qquad (A1.2)$$

$$C_{10} + C_8 \rightleftharpoons C_3 \qquad K_3 \qquad (A1.3)$$

$$C_{11} + C_8 \rightleftharpoons C_4 \qquad K_4 \qquad (A1.4)$$

$$C_{10} + C_7 \rightleftharpoons C_5 \qquad K_5 \qquad (A1.5)$$

$$C_{11} + C_7 \rightleftharpoons C_6 \qquad K_6 \qquad (A1.6)$$

These conditions lead to[14]:

$$
\begin{array}{c}
 \\
\text{(A1.1)} \\
\text{(A1.2)} \\
\text{(A1.3)} \\
\text{(A1.4)} \\
\text{(A1.5)} \\
\text{(A1.6)}
\end{array}
\begin{array}{c}
\begin{array}{ccccccccccc} C_1 & C_2 & C_3 & C_4 & C_5 & C_6 & C_7 & C_8 & C_9 & C_{10} & C_{11} \end{array} \\
\begin{pmatrix}
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 1 \\
-1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 1 & 0 & -1 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & -1
\end{pmatrix}
\end{array}
\begin{pmatrix}
\bar{C}_1 \\ \bar{C}_2 \\ \bar{C}_3 \\ \bar{C}_4 \\ \bar{C}_5 \\ \bar{C}_6 \\ \bar{C}_7 \\ \bar{C}_8 \\ \bar{C}_9 \\ \bar{C}_{10} \\ \bar{C}_{11}
\end{pmatrix}
=
\begin{pmatrix}
\bar{K}_1 \\ \bar{K}_2 \\ \bar{K}_3 \\ \bar{K}_4 \\ \bar{K}_5 \\ \bar{K}_6
\end{pmatrix}
\qquad \text{(A1.7)}
$$

This equation can be rearranged by subtracting (A1.1) from (A1.2) and multiplying (A1.1) with -1 which leads to:

$$
\begin{pmatrix}
\bar{C}_1 \\ \bar{C}_2 \\ \bar{C}_3 \\ \bar{C}_4 \\ \bar{C}_5 \\ \bar{C}_6
\end{pmatrix}
=
\begin{pmatrix}
0 & 0 & 1 & -1 & 1 \\
0 & 0 & 1 & 1 & -1 \\
0 & 1 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 & 1 \\
1 & 0 & 0 & 1 & 0 \\
1 & 0 & 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\bar{C}_7 \\ \bar{C}_8 \\ \bar{C}_9 \\ \bar{C}_{10} \\ \bar{C}_{11}
\end{pmatrix}
+
\begin{pmatrix}
-\bar{K}_1 & \\
\bar{K}_1 & -\bar{K}_2 \\
\bar{K}_3 & \\
\bar{K}_4 & \\
\bar{K}_5 & \\
\bar{K}_6 &
\end{pmatrix}
\qquad \text{(A1.8)}
$$

or

$$
\bar{C}_D = M \cdot \bar{C}_I + \bar{K} \qquad \text{(A1.9)}
$$

where the abbreviations D and I are used for dependent and independent

The conditions which derive from mass, charge and atom conservation are:

$$
\begin{aligned}
G_1 &= C_1 + C_2 + C_9 && \text{(A2.1)} \\
G_2 &= C_3 + C_4 + C_5 + C_6 + C_{10} + C_{11} && \text{(A2.2)} \\
G_3 &= C_3 + C_4 + C_8 && \text{(A2.3)} \\
G_4 &= C_5 + C_6 + C_7 && \text{(A2.4)} \\
r &= \frac{2C_2 + C_3 + C_5 + C_9 + C_{10}}{2G_1 + G_2} && \text{(A2.5)}
\end{aligned}
$$

From these conditions we have to calculate C_I. By simple algebraic manipulation we get:

$$
\begin{aligned}
C_7 &= G_1 V_4 - C_5 - C_6 && \text{(A2.6)} \\
C_8 &= G_1 V_3 - C_3 - C_4 && \text{(A2.7)} \\
C_9 &= G_1 - C_1 - C_2 && \text{(A2.8)} \\
C_{10} &= G_1[(2+V_2)r - 1] + C_1 - C_2 - C_3 - C_5 && \text{(A2.9)} \\
C_{11} &= G_1[(2+V_2)(1-r) - 1] - C_1 + C_2 - C_4 - C_6 && \text{(A2.10)}
\end{aligned}
$$

These equations can also be written as follows:

$$
\begin{pmatrix}
C_7 \\ C_8 \\ C_9 \\ C_{10} \\ C_{11}
\end{pmatrix}
= G_1
\begin{pmatrix}
V_4 \\ V_3 \\ 1 \\ r(2+V_2) - 1 \\ (1-r)(2+V_2) - 1
\end{pmatrix}
+
\begin{pmatrix}
0 & 0 & 0 & 0 & -1 & -1 \\
0 & 0 & -1 & -1 & 0 & 0 \\
-1 & -1 & 0 & 0 & 0 & 0 \\
1 & -1 & -1 & 0 & -1 & 0 \\
-1 & 1 & 0 & -1 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6
\end{pmatrix}
$$

$$
C_I = N + B \cdot C_D \qquad \text{(A2.11)}
$$

The set of equations which has to be solved is therefore

$$
\begin{aligned}
\bar{C}_D &= M \cdot \bar{C}_I + \bar{K} \\
C_I &= B \cdot C_D + N
\end{aligned}
\qquad \text{(A3)}
$$

Obviously they cannot be solved explicitely and we have to apply an iterative procedure.

We start with reasonable values for C_I, say C_I^i. From these initial values we calculate a first approximation for $C_D = \exp(\bar{C}_D)$ which is called C_D^i.

If C_I^i and C_D^i fulfill the equation (A3), then obviously

$$
C_I^i - [N + B \cdot C_D^i] = g(C_D^i, C_I^i) \qquad \text{(A4.1)}
$$

is equal to zero. Otherwise we have to find a correction for $C_I^{i+1} = C_I^i + \Delta C_I$. This correction can be found by expanding $g(C_D^i, C_I^i)$ into a Taylor series and by taking into account only the first two terms:

$$
g(C_D^i, C_I^i) + \left[\frac{dg}{dC_I}\right] \cdot \Delta C_I = 0 \qquad \text{(A4.2)}
$$

By applying standard matrix calculation it can be shown that the following equation is fulfilled:

$$
\left[\frac{dg}{dC_I}\right] = E_I - B \cdot \mathrm{diag}(C_D) \cdot M \cdot \mathrm{diag}(C_I^{-1}) \qquad \text{(A4.3)}
$$

which means in our case:

$$\left[\frac{dg}{dC_I}\right] = \begin{pmatrix} 1 & & & & & 0 \\ & 1 & & & & \\ & & 1 & & & \\ & & & 1 & & \\ 0 & & & & 1 & \\ & & & & & 1 \end{pmatrix} - \begin{pmatrix} 0 & 0 & 0 & 0 & -1 & -1 \\ 0 & 0 & -1 & -1 & 0 & 0 \\ -1 & -1 & 0 & 0 & 0 & 0 \\ 1 & -1 & -1 & 0 & -1 & 0 \\ -1 & 1 & 0 & -1 & 0 & -1 \end{pmatrix}$$

$$\cdot \begin{pmatrix} C_1 & & & & & 0 \\ & C_2 & & & & \\ & & C_3 & & & \\ & & & C_4 & & \\ & & & & C_5 & \\ 0 & & & & & C_6 \end{pmatrix} \cdot \begin{pmatrix} 0 & 0 & 1 & -1 & 1 \\ 0 & 0 & 1 & 1 & -1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1/C_7 & & & & & \\ & 1/C_8 & & & & \\ & & 1/C_9 & & & \\ & & & 1/C_{10} & & \\ & & & & 1/C_{11} & \end{pmatrix}$$

(A4.4)

With this information ΔC_I is evaluated from (A4.2) by standard methods. The new $C_I^{i+1} = C_I^i + \Delta C_I$ is put into equation (A3) and procedures continue until $g(C_D^{i+n}, C_I^{i+n})$ is considered to be small enough. The whole procedure can be carried out by means of a small computer.

Photostationary state:

In the photostationary state the condition (A1.1) is no more fulfilled. Instead of equation (A1.8) we get:

$$\begin{pmatrix} \bar{C}_2 \\ \bar{C}_3 \\ \bar{C}_4 \\ \bar{C}_5 \\ \bar{C}_6 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 & -1 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \bar{C}_7 \\ \bar{C}_8 \\ \bar{C}_9 \\ \bar{C}_{10} \\ \bar{C}_{11} \\ \bar{C}_1 \end{pmatrix} + \begin{pmatrix} -\bar{K}_2 \\ \bar{K}_3 \\ \bar{K}_4 \\ \bar{K}_5 \\ \bar{K}_6 \end{pmatrix} \qquad (A5)$$

$$\bar{C}_D = M \cdot \bar{C}_I + \bar{K}$$

In the equations (4.1), (4.2) we have defined the partial reduction degree r_1 and r_2. With the symbols used in this appendix r_1 is given by

$$r_1 = \frac{C_9 + 2C_2}{2G_1} \qquad (A6.1)$$

This is our new condition in the photostationary state. Instead of equation (A2.11) we now have to write:

$$\begin{pmatrix} C_7 \\ C_8 \\ C_9 \\ C_{10} \\ C_{11} \\ C_1 \end{pmatrix} = G_1 \begin{pmatrix} V_4 \\ V_3 \\ 2 \cdot r_1 \\ r(2+V_2) - 2r_1 \\ V_2 + 2r_1 - r(2+V_2) \\ 1 - 2r_1 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & -1 & -1 \\ 0 & -1 & -1 & 0 & 0 \\ -2 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & -1 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{pmatrix}$$

$$C_I = N + B \cdot C_D \qquad (A6.2)$$