

ESA SP-240

November 1985

Solar energy '85

Resources – Technologies – Economics

Papers presented at the
Summer School held at Igls, Austria,
organised by ASSA and DFVLR and
sponsored by ESA, BEW & BFR

European space agency / agence spatiale européenne

8-10, rue Mario-Nikis, 75738 PARIS CEDEX 15, France

<i>Proceedings published and distributed by</i>	ESA Publications Division, ESTEC, Noordwijk, The Netherlands
<i>compiled by</i>	W R Burke
<i>printed in</i>	The Netherlands
<i>Price code</i>	E3
<i>International serial number</i>	ISSN 0379 - 6566
<i>Copyright</i>	© 1985 by European Space Agency

PHOTOCHEMICAL, ELECTROCHEMICAL AND THERMOCHEMICAL TRANSFORMATION
AND STORAGE OF SOLAR ENERGY: THERMODYNAMIC ASPECTS

Gion Calzaferri

Inorganic and Physical Chemistry
University of Bern
Freiestrasse 3, CH-3000 Bern 9 (Switzerland)

SUMMARY

Arguments of reversible and irreversible chemical thermodynamics are first explained and then applied to the transfer and storage of chemical and radiation potential. The key processes are identified as watersplitting, carbon dioxide reduction and nitrogen reduction. New results on photochemical storage processes are reported.

First I will treat the question "why chemical transformation and storage?" and then explain the most important possibilities. Many of you might not be familiar with reversible and irreversible chemical thermodynamics. Therefore a large part of this article is dedicated to an introduction of this field. The arguments developed are then used to discuss the transfer and storage of chemical radiation potential from a thermodynamic point of view. Finally I procure some photochemical background knowledge.

2. WHY CHEMICAL TRANSFORMATION AND STORAGE

We all know that one of the severe limitations to applying solar energy technologies on a large scale basis in our environment is that during summer there is more solar energy available than we would need whereas in winter we would need more than is available. The other reasons why storage is so important are day/night alternations and meteorological fluctuations. The rate of production of chemical energy in the natural photosynthesis process is in the order of $4 \cdot 10^{13}$ Watt or 0.023% of solar power on the earth ($1.7 \cdot 10^{17}$ Watt). This corresponds to about 3 times the actual total human need. If we wished to supply 10^{10} human beings with the comfortable share of 4 kW each and if, for that purpose we had a solar energy process with a 10% storage capacity, we should need 1.6×10^6 km² of land close to 30° latitude, which corresponds to 18% of the Sahara. For a storage capacity of 20%, we should need only 9%.

Conclusion: A 10 to 20% solar energy storage process would solve energy problems for ever, so long as the Earth's population did not much exceed the 10^{10} limit, which it is to be hoped will be the case.

Why chemical energy? This question is easy to answer by comparing some energy densities shown in Table 2.1 and Table 2.2.

1. INTRODUCTION

The key processes for chemical transformation and storage of solar energy are watersplitting, carbon dioxide reduction and nitrogen reduction. By now none of these reactions can be carried out directly under solar irradiation. For the last few years photochemists have been making progress, however, and there is little doubt that efficient solar energy storage reactions will be found. Some significant steps have also been made in our laboratory. Actually the only possibility for chemical storage of solar energy is first producing electricity, preferably by photovoltaic devices, and then electrolyzing water to produce hydrogen. Although the mentioned key processes are the most preferable for chemical transformation and storage of solar energy, there are many photoreactions which could potentially lead to valuable products in a chemical solar industry. Engineering of solar reactors is in progress and we are soon expecting first devices for the production and storage of interesting chemicals.

In this article I do not describe any of these reactions but I concentrate on the storage problem.

Table 2.1.

10⁴kWh energy stored in different systems.

Chemical energy: 1 m³ oil
3 m³ NH₃

Electrochemical: 600 m³ lead/acid
40 m³ Zn/air

Latent heat: 10 m³ NaF/CaF₂/MgF₂ at 800°C

Sensible heat: 250 m³ of warm water at 90°C
used at 60°C

Mechanical: Fly wheel:
3 tons spinning at 10⁴ t/min
(R = 5m)
Hydro-Electric:
3600 m³ of water at Δh = 1000 m

Table 2.2.

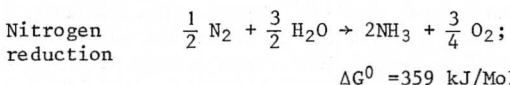
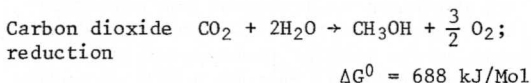
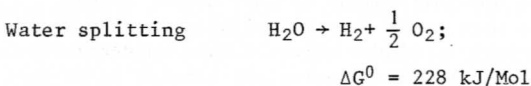
Energy density of some fuels

Substance	[kWh/kg]	[kWh/m ³]
Hydrogen	34-40	3.3 gas
		2300 liquid
Methane	18-20	10-11 gas
Aethanol	7.5-8.3	6·10 ³ -6.6·10 ³
Gasoline	11.7-12.8	8.4x10 ³
Mineral Coal	7.6-9.7	20 000
Wood	4-5	5 000

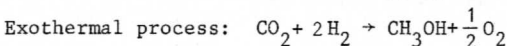
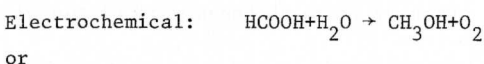
All our fuels consist of stored chemical energy. They are burned with oxygen from the air. It would be far more economic to use them in fuel cells.

3. MOST IMPORTANT POSSIBILITIES

The most important solar energy storage processes are (all compounds in gaseous phase):



Probably, carbon dioxide reduction to methanol and nitrogen reduction cannot be achieved in one step. As an example, the carbon dioxide reduction could be carried out in one of the following ways:



The electrical energy needed in both processes could be supplied by photovoltaic cells.

4. CHEMICAL THERMODYNAMICS; A VERY SHORT INTRODUCTION

The difference between chemical thermodynamics and thermodynamics used in physics or engineering science is that in chemical thermodynamics the most important variables of the state functions are the concentrations of the chemical species n_i . I will therefore try to summarise the necessary notions, so that people who are less familiar with chemical thermodynamics will be able to follow the most important conclusions.

Energy and enthalpy changes in chemical reactions:

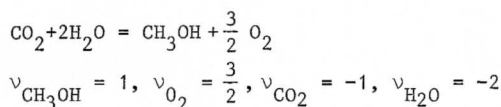
Suppose that we consider a general chemical reaction



This is often more conveniently written as an algebraic equation with all terms on one side,

$$\ell L + mM + \dots - aA - bB - \dots = \sum_{i=1}^r \nu_i X_i = 0 \quad (4.2)$$

where the symbols X_i stand for the r species A, B, ... and the ν_i are the stoichiometric coefficients a, b, \dots . By convention we always subtract the reactants from products, so that ν_i must be positive for the products and negative for the reactants. Example



How do we go from an equation in terms of chemical formulas to one involving the thermodynamic properties of substances? Consider the process by which we balance a chemical equation. What we actually do is apply the principle that the atoms of each element are conserved in chemical processes. But mass is also conserved. We can therefore write, for the change of mass in a reaction,

$$\Delta M = \sum_{i=1}^r \nu_i M_i = 0 \quad (4.3)$$

where M_i is the molar mass of substance i . Now consider the internal energy and the enthalpy. They are state functions, and thus defined for any thermodynamic state of the system. Furthermore, they are extensive functions*), so that we can define an energy or enthalpy per mole. We can therefore write equations similar to eq (4.3) for the total changes in internal energy and enthalpy in a reaction.

*)

An extensive parameter, such as volume and mass depends on the size of the system as a whole and on the amounts of the various substances present. Intensive parameters, such as pressure, temperature and concentrations, which have definite values at each point in the system and do not depend on the size.

$$\Delta U = \sum_{i=1}^r v_i u_i \quad (4.4)$$

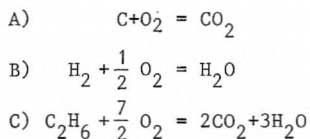
$$\Delta H = \sum_{i=1}^r v_i h_i$$

If u_i and h_i are the internal energy and enthalpy per mole of component i , respectively, then the ΔU and ΔH defined by these equations refer to 1 mole of the stoichiometric reaction.

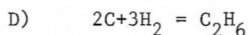
But what are the states for which u_i and h_i are defined? To specify ΔU and ΔH for a reaction, we must clearly know not only the stoichiometric equation but the initial states of the reactants and the final states of the products. By "state" we mean such things as the temperature and pressure; u_i and h_i in eq. (4.4) refer to the initial state for the reactants and to the final state for the products. An additional complication is the fact that changes in energy and enthalpy occur even when substances are mixed without reaction. Since in practice chemical processes are usually directed to the production of pure substances, it is customary to take the initial state as consisting of pure reactants isolated from one to another, and the final state as isolated pure products. One can then imagine the overall reaction as a three-step process:

- Take the pure reactants in their initial equilibrium states, and physically mix them under reaction conditions.
- Allow the reaction to proceed.
- Isolate the individual products from the reaction mixture and bring them to their final equilibrium states.

Since a set of chemical equations can be thought of as a set of mass balances, it follows that different equations can be combined by addition and subtraction to obtain any desired mass balance. It does not matter whether or not the final equation represents a real chemical reaction, that is, one observed in the laboratory. For an example of this consider the several reactions:



If we algebraically add 2(eq. A)+3(eq. B)-(eq. C), multiplying each equation by the indicated numerical factor, we obtain the composite reaction

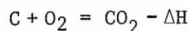


But what good is such a manipulation? The answer is that it is equally valid for extensive quantities other than mass. Until now we have thought of a substance's chemical formula as representing the substance itself, or in stoichiometric contexts a mole of the substance; but it can equally well represent the internal energy, enthalpy or any other extensive property of a mole of the substance. Let us examine this. The enthalpy balance for eq.

A) above can be written as

$$h_{\text{C}} + h_{\text{O}_2} = h_{\text{CO}_2} - \Delta H$$

or in the more usual short hand (compare Section 3)



and for reaction D):

$$-2\Delta H_{\text{A}} - 3\Delta H_{\text{B}} + \Delta H_{\text{C}} = -\Delta H_{\text{D}}$$

$$\Delta H_{\text{D}} = 2\Delta H_{\text{A}} + 3\Delta H_{\text{B}} - \Delta H_{\text{C}}$$

We now want to calculate the enthalpy and internal energy changes in chemical reactions as functions of temperature and volume or pressure.

Remember that for constant composition:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

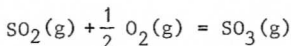
$$\Delta U = U(T_2, V_2) - U(T_1, V_1) = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} \left\{ T \left(\frac{\partial P}{\partial T}\right)_V - P \right\} dV \quad (4.5)$$

and

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Delta H = H(T_2, P_2) - H(T_1, P_1) = \int_{T_1}^{T_2} C_p dT + \int_{P_1}^{P_2} \left\{ V - T \left(\frac{\partial V}{\partial T}\right)_P \right\} dP$$

Suppose that we know the heat of reaction for



at 291 K and 1 atm. What is the heat of reaction at 873 K and 1 atm?

Now, the "heat of reaction" is just the difference between the enthalpies of products and reactants. Once ΔH is known at one T and P , it can be obtained at any other T and P by applying eq (4.5) to each of the substances involved:

$$\Delta H_{\text{reac}}(T_2, P_2) = \sum_i v_i h_i(T_2, P_2)$$

$$= \Delta H_{\text{reac}}(T_1, P_1) + \sum_i v_i \left\{ \int_{T_1}^{T_2} C_p dT + \int_{P_1}^{P_2} \left[v_i - T \left(\frac{\partial v_i}{\partial T}\right)_P \right] dP \right\} \quad (4.6)$$

(For a perfect gas the pressure integrals vanish, because

$$v_i = T \left(\frac{\partial v_i}{\partial T}\right)_P .)$$

Let us now return to the specific example given above and actually carry out the calculations. Since P_1 and P_2 are the same, the pressure integrals drop out. The other data we need are:

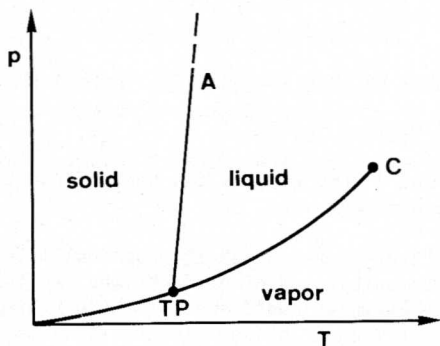
$$\begin{aligned}
 H(291\text{K}, 1\text{atm}) &= -5351 \text{ J/mole} \\
 C_p(\text{SO}_2) &= 2.72 + 4.1 \cdot 10^{-4}T - 4.89 \cdot 10^{-6}T^{-2} \\
 C_p(\text{O}_2) &= 1.8 + 1.93 \cdot 10^{-4}T - 2.1 \cdot 10^{-6}T^{-2} \\
 C_p(\text{SO}_3) &= 3.02 + 1.53 \cdot 10^{-3}T
 \end{aligned}$$

Substitution and integration over T then gives

$$\begin{aligned}
 \Delta H(873\text{K}, 1\text{atm}) &= \Delta H(291\text{K}, 1\text{atm}) + \int_{291}^{873} [C_p(\text{SO}_3) - C_p(\text{SO}_2) \\
 &\quad - \frac{1}{2} C_p(\text{O}_2)] dT \\
 &= -5351 + \int_{291}^{873} [-0.6 + 1.02 \cdot 10^{-3}T \\
 &\quad + 5.94 \cdot 10^{-6}T^{-2}] dT \\
 &= -5291 \text{ J/Mole}
 \end{aligned}$$

Introduction to phase changes:

A phase is a region within which all the intensive variables vary continuously, whereas at least some of them have discontinuities at the borders between phases. For example, ice and water in equilibrium form a two-phase system. By a phase change we mean simply the process that brings a system from a state characterized as phase A to another state characterized as phase B. The transition from water to ice or from water to vapor is an example of a phase change.



Although phase changes in systems with several components can be quite complicated, as an introduction it is sufficient to discuss a one component system. For any pure substance, a (P,T) diagram shows the various phases as distinct regions separated by sharp boundaries. A process that involves a phase change corresponds to a path crossing of one of these boundaries. The phase change itself occurs entirely at the point where the path crosses the boundary, and thus at constant temperature and pressure. In all ordinary phase changes (freezing, vaporization etc.) there is a difference in density between the two phases involved. The amount of heat absorbed or released in a phase change is called the latent heat.

To illustrate these concepts, suppose that our system is pure water and our path is the isobar $p=1\text{atm}$. We start with a piece of ice at some temperature below 0°C and gradually add heat. The ice increases

in temperature and expands slightly until 0°C is reached. At this point the ice transforms continuously to liquid water, at constant temperature and pressure, with 6 007 kJ absorbed for each Mol of H_2O melted. After all ice is transformed to liquid, adding more heat will raise the temperature again.

In general, whenever the path a system follows from state P_1, T_1 to state P_2, T_2 crosses a phase boundary, the latent heat of the transition must be included in ΔH for the process. Thus, consider the above example of the 1-atm ice \rightarrow water transition. The molar enthalpy change must be calculated as (l = liquid, s = solid):

$$h(l, T_2) - h(s, T_1) = \int_{T_1}^{0^\circ\text{C}} C_p(s) dT + \Delta h_{\text{fus}} + \int_{0^\circ\text{C}}^{T_2} C_p(l) dT \quad (4.7)$$

Standard States

The change in internal energy or enthalpy for a given process measures only the relative properties of the initial and final states. Not only do absolute values of energy and enthalpy not need to be specified, but it is meaningless even to speak of "absolute" values, because the zero of energy is arbitrary. It is convenient, however, to have definite reference points to which energy and enthalpy of substances can be related, because the values so defined can then be tabulated for substances rather than reactions. The choice of such reference states is arbitrary. Once such choices have been made, however, they must be consistently used throughout a given set of calculations. For pure substances it is conventional to choose standard states in the following way:

1. The standard state of a chemical substances at a given temperature is taken to be a state of the pure compound or element at that temperature and pressure of 1 atm. If no temperature is specified, 25°C is to be assumed.
2. Each element in its most stable form at 25°C and 1 atm is assigned an enthalpy of zero.

Thermodynamic quantities referring to a standard state are designated by the superscript 0 . Thus the standard heat of reaction, the value of ΔH for a reaction in which all the reactants and products are in standard states at the same temperature T is designated as ΔH^0 or ΔH_T^0 . We can now rigorously define the standard heat of formation ΔH_f^0 for the reaction in which a compound is formed from its elements in their most stable forms. The values of ΔH_f^0 have been tabulated for a very large number of compounds, usually at 25°C ; a sampling is included in Table 4.1.

Table 4.1

ΔH_f^0 standard heat of formation of a given substance from its elements at 25°C [kcal/Mol]

S^0 the entropy of the given substance in its thermodynamic reference state at the reference temperature 25°C [cal/deg Mol]

c = cristalline, g = gaseous, l = liquid, aq = aqueous

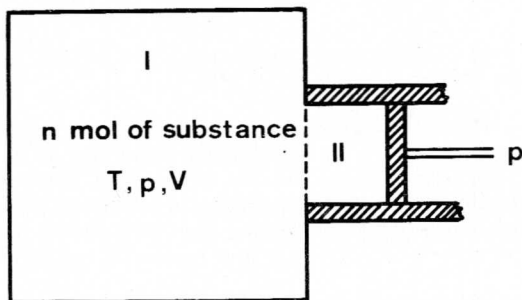
Substance	state	ΔH_f^0	ΔS^0
NH ₃	l	-11.04	46.01
N ₂ H ₄	l	12.10	28.97
N ₂ H ₄	aq	8.16	33
CH ₄	g	-17.89	44.50
C ₂ H ₆	g	-20.24	54.85
C ₃ H ₈	g	-24.82	64.85
H ₂ O	g	-57.8	45.1
H ₂ O	l	-68.3	16.7
CO ₂	g	-94.05	51.06
HCOOH	aq	-101.68	39
CH ₃ OH	l	-57.04	30.3
CH ₃ CH ₂ OH	l	-66.36	38.4
H ₂ S	g	-4.93	49.16
H ₂ S	aq	-9.5	29

Given our specification of the standard enthalpy of elements it is clear that for any species at 25°C the standard enthalpy H^0 has the same value as ΔH_f^0 (25°C). Since the same elements appear on both sides of any chemical reaction equation, it is obvious that the standard enthalpy change in any reaction can be obtained directly from the standard heats of formation of all the species involved:

$$\Delta H_{\text{reac}}^0 = \sum_{i=1}^r \nu_i h_i = \sum_{i=1}^r \nu_i (h_i^0 - h_{i,\text{elements}}^0) = \sum_{i=1}^r \nu_i \Delta H_f^0(i) \quad (4.8)$$

Gibbs free energy G and chemical potential μ_i

To introduce the chemical potential we must understand how the thermodynamic functions of the system depends on its mass.



Consider a closed system with two parts, I and II. In part I, with volume V, there are n mole of a pure substance at temperature T and pressure p; in part II there are dn mole of the same substance at the same pressure and temperature, and occupying volume vdn, where v is the molar volume. Let the boundary between part I and the surroundings be deformable in such a way that as V varies, the pressure of the substance inside remains equal to the external pressure. Finally, let there be an insulated piston connected to II so that external work can be done on the dn mol of substance in that part of the system. The boundary between parts I and II is permeable to matter.

We consider two states of the total system. In the initial state of the system the dn mol of substance in part II are outside the envelope defining the volume of part I. The internal energy of the total closed system is then

$$nu+udn$$

where u is the molar internal energy of the substance. In the final state of the system the dn mol of substance in part II have been isothermally and reversibly driven at constant pressure p into part I, whose volume thereby changes from V to V+dV. In this change of state the surroundings coupled to the piston do work $pv \cdot dn$ on the system, the expansion of part I does work +pdV on the surroundings, and heat \bar{dq} is transferred to part I from the surroundings. Let the internal energy in the final state be denoted by

$$nu+dU.$$

The difference in internal energy according to the first law is

$$nu+dU-(nu+udn) = dU-udn = \bar{dq}-pdV+pvdn \quad (4.9)$$

Using the definition of the molar enthalpy,

$$h = u+pv \quad (4.10)$$

we find for the internal energy change of part I,

$$dU = \bar{dq}+hdn-pdV \quad (4.11)$$

Consider now the form taken by the second law when mass transfer is permitted. In the initial state of the system described above the entropy is

$$ns+sdn$$

where s is the molar entropy. In the final state the entropy is denoted by

$$\bar{ns}+dS$$

As a result of the process by which the dn mol of substance are added to part I, there are entropy changes associated with the mass transfer, the work done, and the heat transferred. Since the dn mol of substance were added to part I isothermally and reversibly, the change in entropy of the total system, $dS-sdn$, is

$$dS-sdn = \frac{\bar{dq}}{T} = \frac{dU}{T} - \frac{h}{T} dn + \frac{P}{T} dV \quad (4.12)$$

Using the definition of the molar Gibbs free energy

$$g = h-Ts \quad (4.13)$$

we find

$$dU = TdS-pdV+gdn \quad (4.14)$$

The molar Gibbs free energy of a pure substance is also called the chemical potential μ of that substance.

Most systems of chemical interest contain more than one component. In the presence of several components we get instead of (4.14)

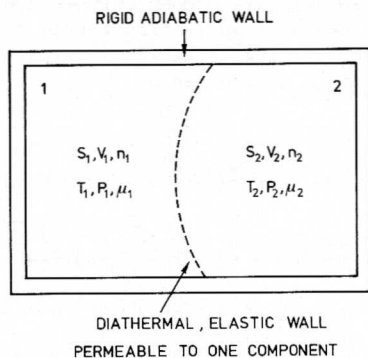
$$dU = TdS-pdV+ \sum_{i=1}^r \mu_i dn_i \quad (4.15)$$

and for the Gibbs free energy we have

$$G = U-TS+pV = \sum_{i=1}^r n_i \mu_i$$

5. IRREVERSIBLE PROCESSES

The system we consider is enclosed by a rigid adiabatic wall. The two compartments are separated by a diathermal, elastic barrier that is permeable to one of the components in the system.



The change in the entropy of the compartments is given by the sum of the partial changes due to the transport of energy, volume and matter:

$$dS = \frac{\partial S_1}{\partial U_1} dU_1 + \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_1}{\partial n_1} dn_1 + \frac{\partial S_2}{\partial U_2} dU_2 + \frac{\partial S_2}{\partial V_2} dV_2 + \frac{\partial S_2}{\partial n_2} dn_2 \quad (5.1)$$

Since the total energy, volume, and amount of substance are constants,

$$dU_1 = -dU_2, \quad dV_1 = -dV_2, \quad dn_1 = -dn_2$$

Introducing these conditions into (5.1) we obtain

$$dS = dU_1 \left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} \right) + dV_1 \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right) + dn_1 \left(\frac{\partial S_1}{\partial n_1} - \frac{\partial S_2}{\partial n_2} \right) \quad (5.2)$$

By using the relations

$$\left(\frac{\partial S}{\partial U} \right)_{V,n} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V} \right)_{U,n} = \frac{P}{T}, \quad \left(\frac{\partial S}{\partial n} \right)_{U,V} = -\frac{\mu}{T}$$

equation (5.2) becomes

$$dS = dU_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + dV_1 \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) - dn_1 \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \quad (5.3)$$

This equation shows that the entropy increase in our system is given by the sum of products of changes in the three internal parameters, U , V , and n multiplied by suitable affinities, $(1/T_1 - 1/T_2)$, $(P_1/T_1 - P_2/T_2)$ and $(\mu_1/T_1 - \mu_2/T_2)$. It is of interest to examine the last term in eq. (5.3) when $T_1 = T_2$ and $P_1 = P_2$. In this case,

$$dS = -dn_1 \frac{\mu_1 - \mu_2}{T} > 0 \quad (5.4)$$

If $\mu_1 > \mu_2$, dn_1 must be negative and matter will be transported from the higher to the lower chemical potential. This justifies the term "chemical potential", since the gradient of this quantity acts as the driving force for the transport of matter.

dS will become zero when $\mu_1 = \mu_2$; this is the condition for chemical equilibrium.

Equation (5.3) may be cast in another form, which will be useful. Let us denote the bracketed differences in this equation by Δ so that

$$\Delta \left(\frac{1}{T} \right) = \frac{1}{T_1} - \frac{1}{T_2}; \quad \Delta \left(\frac{P}{T} \right) = \frac{P_1}{T_1} - \frac{P_2}{T_2}; \quad \Delta \left(\frac{-\mu}{T} \right) = - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right)$$

Further let us divide both sides of eq. (5.3) by the time change dt , and denote the flow of energy dU_1/dt by J_U , the flow of volume dV_1/dt by J_V , and the flow of matter dn_1/dt by J_n . Equation (5.3) may then be written as:

$$\frac{dS}{dt} = J_U \Delta \left(\frac{1}{T} \right) + J_V \Delta \left(\frac{P}{T} \right) + J_n \Delta \left(\frac{-\mu}{T} \right) \quad (5.5)$$

This equation demonstrates clearly, that the rate of entropy production in adiabatic irreversible processes is the sum of the products of individual flows each multiplied by the corresponding affinity.

6. TRANSFER AND STORAGE OF CHEMICAL AND RADIATION POTENTIAL

We have now the necessary background to study the thermodynamic losses in chemical storage reactions. Consider a chemical reaction step in which products B, at chemical potential μ_B are formed from reactants A at chemical potential μ_A .



The rate of storage of chemical potential per unit volume in the product B is $j \cdot \mu_B$.

$$j = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = \text{rate of change of concentration in the forward reaction } A \rightarrow B$$

$J_f = k_f[A]$; $J_b = k_b[B]$ k_f and k_b are the rate constants for the forward and for the backward reaction.

In Section 5, eq. (5.4), we have seen that if the forward reaction proceeds at a finite rate $j > 0$, there is a net entropy production and $\mu_B < \mu_A$. At equilibrium $j = 0$ and in the limit of $j = \text{max}$ the rate of storage of chemical potential $j \cdot \mu_B$ is equal zero because μ_B is equal zero. There must be some intermediate finite rate of reaction at which the power has a maximum value.

The scheme (6.1) corresponds to the steady state condition: the injection of A into the system exactly equals the removal of B from the system. We will assume that no external work is done. Because the chemical potentials μ_X can be written in the form $\mu_X = \mu_X^0 + RT \ln[X]$ the change in chemical potential is given by

$$\Delta \mu = \mu_B - \mu_A = (\mu_B^0 - \mu_A^0) + RT \ln \frac{[B]}{[A]} \quad (6.2)$$

Because $\mu_B^0 - \mu_A^0$ is equal to $-RT \ln K$, K is the equilibrium constant and K is equal to k_f/k_b and j is equal to $J_f - J_b$ we get

$$\Delta\mu = RT \ln\left(\frac{k_b[B]}{k_f[A]}\right) = RT \ln(1-j/J_f) \quad (6.3)$$

For a sequence of l reactions of this type, with a common flux j , there will be an overall loss of chemical potential given by

$$\Delta\mu = RT \sum_1 \ln\left(1 - \frac{j}{J_f(1)}\right) \quad (6.4)$$

According to equation (5.5) the entropy production is equal to

$$\frac{dS}{dt} = j R \sum_1 \ln\left(1 - \frac{j}{J_f(1)}\right) > 0 \quad (6.5)$$

For the rest we limit the discussion to the case $l = 1$. The rate P of production of chemical potential in the form of product B at chemical potential μ_B is given by

$$P = j\mu_B = j(\mu_A + \Delta\mu) \\ P = j[\mu_A + RT \ln(1 - \frac{j}{J_f})] \quad (6.6)$$

When the flux j to give maximum power, $(dP/dj)_J = 0$. Differentiating (6.6) with respect to j and setting the derivative equal to zero gives

$$\frac{j_m/J_f}{1-j_m/J_f} - \ln(1-j_m/J_f) = \frac{\mu_A}{RT} \quad (6.7)$$

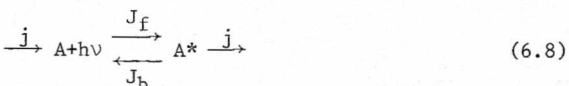
j_m is the flux at maximum power. The free-energy transfer efficiency η is defined as $\eta = \mu_B/\mu_A = (1 + \Delta\mu/\mu_A)$. Example: $\mu_A = 1$ eV leads to

$$\frac{\mu_A}{RT} = 38.7, \quad \frac{j_m}{J_f} = 0.972, \quad -\Delta\mu = 0.093 \text{ eV}$$

$$\text{and } \eta_m = 0.907$$

This means that under maximum power conditions the entropy production leads to a loss of approximately 10% when the chemical potential to be transferred is 1 eV.

For a photochemical reaction without leakage as shown in (6.7) the first product becomes the excited state A^* .



The potential of the "reactants" is composed of the chemical potential of A and the potential of the light quanta absorbed. Following G. Porter we will call μ_R the radiation potential or the partial molar quantal free energy of the radiation, by analogy with the chemical potentials, and define it as the maximum work which can be derived from one einstein of the quanta when they are absorbed at the ambient temperature T_A . The entropy production in the absorption process is

$$\frac{dS}{dt} = j \cdot \frac{\mu_A + \mu_R - \mu_A^*}{T} = jR \ln(1-j/J_f) \quad (6.9)$$

In any realistic transformation and storage process for solar energy conversion, we have to assume that the direction of the radiation beam is lost. This is equivalent to scattering the radiation from angle Ω to 4π . Including this entropy production and approximating the solar energy distribution as a blackbodyradiation, the overall efficiency of solar energy conversion into chemical potential at maximum power is

$$\eta_m = \frac{(\mu_A^* - \mu_A)\lambda}{NhC} = 1 - \frac{T_A}{T_R} - \frac{RT_A\lambda}{NhC} \ln \frac{4\Omega}{\pi} \\ + \frac{RT_A\lambda}{NhC} \ln\left(1 - \frac{j_m}{J_f}\right) \quad (6.10)$$

T_R = effective temperature of the radiation, T_A = temperature of A, N = Avogadro number, h = Planck's constant, C = speed of light, λ = wavelength of light. From this the overall efficiency at maximum power for light quanta 700 nm is calculated to be 0.71.

Although the other wavelengths in the sun's spectrum will, because the sun approximates to a black body, give similar temperatures and therefore similar efficiencies on the basis of (6.10), this calculation has assumed that the energy of the absorbed quantum is exactly equal to the energy E of the excited state. But when a single absorber is used allowance must be made for losses due to non-absorption or the degradation of energy in excess of the zero-point excitation. Two types of single-threshold devices have been studied:

Single absorber with a threshold excitation wavelength λ_0 so that the yield

$$\Phi_A^* = 1 \text{ for } \lambda < \lambda_0 \text{ and } \Phi_A^* = 0 \text{ for } \lambda > \lambda_0$$

The energy of all photons absorbed, after degradation of excess vibrational energy, is hc/λ_0 and the fraction θ of the energy absorbed from a polychromatic source which is available in photochemical change is given by

$$\theta = \frac{\int_{\lambda=0}^{\lambda=\lambda_0} E_\lambda \frac{\lambda}{\lambda_0} d\lambda}{\int_{\lambda=0}^{\lambda=\infty} E_\lambda d\lambda}$$

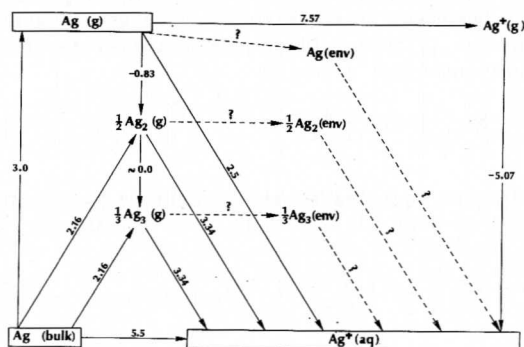
where E_λ is the energy of the radiation in wavelength interval $d\lambda$. For a threshold wavelength of 700 nm and A.M.1, the fraction $\theta = 0.38$, giving an overall solar efficiency at this wavelength of $0.38 \times 0.71 = 0.27$

Hot-carrier solar energy converters: (R.T. Ross and A.J. Nozick)

A single-threshold quantum-utilizing device in which the excited carriers thermally equilibrate among themselves, but not with the environment, can convert solar energy with an efficiency approaching that of an infinite-threshold device. Such a hot-carrier flat-plate device operated under typical terrestrial conditions (AM 1.5 illumination, 300 K) can convert solar energy with an

efficiency of 66%, substantially exceeding the 33% maximum efficiency of a quantum device operating at thermal equilibrium, and the 52% maximum efficiency of an ideal thermal conversion device. This high efficiency is achieved in part through an unusual inversion, in which the chemical potential of the excited electronic band is below that of the ground band. This negative potential difference reduces radiation losses, permitting a low threshold energy, and a high Carnot efficiency resulting from a high carrier temperature.

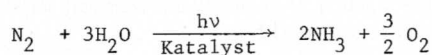
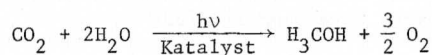
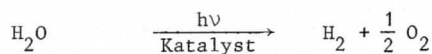
Finally I would like to add an enthalpy diagram which gives interesting information about the reduction capabilities of silver clusters. This diagram illustrates, that the enthalpy and the free energy of clusters can differ very much from the bulk material. A fact which is often misunderstood. In this diagram the enthalpy in condensed phase is related to the heat of hydration of the gaseous Ag^+ ion -5.07 eV.



Enthalpy diagram; env. = environment

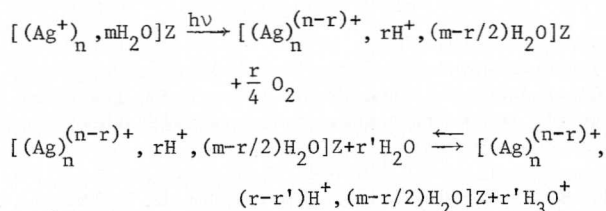
6. KEY PROBLEM IN PHOTOCHEMICAL CONVERSION AND STORAGE OF SOLAR ENERGY

I have already mentioned that watersplitting, reduction of CO_2 and reduction of N_2 are the most preferable solar energy storage processes. In photochemical terms this means the following reactions

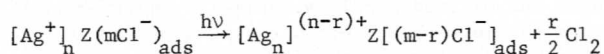


In each case oxygen must be produced. But photo-oxygen evolution with visible light was an unresolved problem in an energetically uphill system noncontaining any electrodes. Recently we have detected selfsensitization of photo-oxygen as well as of photo-chlorine evolution in Ag^+ zeolites. Depending on the conditions O_2 or Cl_2 can be produced over the whole visible spectrum. This means that we have been able to make a considerable step forward in the problem photochemical conversion and storage of solar energy.

From our present knowledge, the overall stoichiometry of this photo-oxygen generation



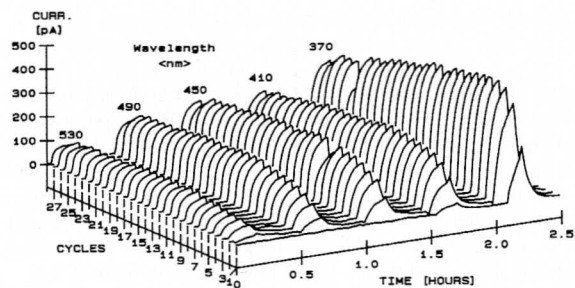
The stoichiometry of the photochlorine evolution below pH4 is



In the figure below a selfsensitization experiment of an aqueous Ag^+ zeolite A dispersion is shown (1 nA*s corresponds to 3.94 nl of oxygen). Energy flux: 9.1 mW/35 cm. Automatic pH control 6-6.3.

LITERATURE USED TO PREPARE THIS ARTICLE

1. Berry, Rice, Ross, *Physical Chemistry*, John Wiley & Sons, New York, 1980.
2. Prigogine I, *Thermodynamics of Irreversible Processes*, Interscience, New York, 1955.
3. Porter G, *J. Chem. Soc. Faraday Trans.*, 2, 79 (1983) 473.
4. Ross R T and Hsiao Ta-Lee, *J. Appl. Phys.*, 48 (1977) 4783.
5. Ross R T and Nozik A J, *J. Appl. Phys.*, 53 (1982) 3813.
6. Calzaferri G, "Photochemical Conversion and Storage of Solar Energy", Ed. J. Rabani, *The Weizmann Science Press*, 1982, p 81-113.
7. Schumacher E, *Chimia*, 32 (1978) 193.
8. Calzaferri G, Hug S, Hugentobler Th and Sulzberger B, *Journal of Photochemistry*, 26 (1984) 109.
9. Calzaferri G and Forss L, in preparation.
10. Calzaferri G and Spahni W, in preparation.



Selfsensitisation experiments