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Thermodynamics of fuel synthesis

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two solvents is then independent of the nature of the para substituent, as shown in

$$\nu_{\max}(\text{MC}) - \nu_{\max}(\text{Me}_2\text{SO}) = \nu_0(\text{MC}) - \nu_0(\text{Me}_2\text{SO}) + \delta\nu(\text{ion pairing}) \quad (13)$$

Values of ν_{\max} are included in Table I. The precision is 2 cm^{-1} . For the Ph-S stretch, ν_{\max} is practically independent of solvent and substituents. For the S-O₃ stretch (where ν_{\max} is measured at the low-frequency maximum), there is significant variation. In Me₂SO, ν_{\max} varies with the p-X substituent but is independent of the cation, as expected for dissociated ions. The variation with p-X is nearly linear with the Hammett substituent constant σ . In CH₂Cl₂, ν_{\max} is reduced. Within the experimental error the reduction is independent of the para substituent but depends on the nature of the cation. This is in agreement with (13) in which $\delta\nu(\text{ion pairing})$ appears as a variable but $\nu(\text{p-substit})$ does not. For R = Me the reduction is $11 \pm 1\text{ cm}^{-1}$ for three different X. For R = Et the reduction is $8 \pm 1\text{ cm}^{-1}$ for four different X and 9 cm^{-1} for three different Y.

One expects from the dielectric constant ($\epsilon = 8.93$ at 25°C) that free-ion concentrations in CH₂Cl₂ are relatively small. Actual free-ion fractions were estimated from conductivity measurements on solutions of *N*-ethyl-*N,N*-dimethylanilinium *p*-X-benzene-sulfonate, X = CH₃, Br. Equivalent conductivities were taken from the work of Denison and Ramsey,²⁵ by applying modest

corrections for differences in viscosity and ionic strength. At 0.03 M electrolyte, the free-ion fraction was 0.010 for X = CH₃ and 0.013 for X = Br. Extrapolation to infinite dilution gave the following association constants for ion-pair formation: For X = CH₃, $K_a = 2.0 \times 10^6\text{ M}^{-1}$. For X = Br, $K_a = 0.9 \times 10^6\text{ M}^{-1}$. These constants should be regarded as tentative estimates but are of a plausible magnitude; by comparison, K_a for *N,N,N*-trimethyl-*p*-toluidinium perchlorate is 4×10^5 in ethylene chloride ($\epsilon = 10.23$) and 5×10^4 in ethylidene chloride ($\epsilon = 9.90$).²⁵ On the other hand, constants deduced recently by a photochemical kinetic method for certain ion pairs in CH₂Cl₂ are considerably smaller.²⁶

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Supplementary Material Available: Details of the concentric spherical dielectric cells used in this work (Figures 7-10) (7 pages). Ordering information is given on any current masthead page.

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On the Thermodynamics of Fuel Synthesis

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An expression for the thermodynamic efficiency of fuel synthesis is derived and applied to elementary examples from thermochemistry, photochemistry, biochemistry, and electrochemistry.

I. Introduction

During the past decade many processes and devices for fuel synthesis and solar energy conversion have been proposed. A computer program which generates new thermochemical cycles for hydrogen synthesis has been reported.¹ Hundreds of thermochemical cycles have been proposed so far,²⁻⁴ and new cycles continue to appear in the literature. Moreover, thermochemical methods represent only a small area of fuel synthesis research; there remain photochemical, biochemical, electrochemical, and several other approaches to fuel production. In the long run at most only a handful of processes are expected to survive to the point of industrial application. From the point of view of technology assessment, detailed prototype evaluation is too time consuming and expensive to be applied to each new process. A preliminary selection procedure is needed that is based on criteria that can be established quickly and cheaply.

One criterion in the technological assessment is the energy efficiency of the process. Although this is strictly a thermodynamic

problem, often thermodynamic analysis provides only an upper bound on the efficiency based upon reversible processes. The reversible limit may be so far from actual operating conditions that its bounds on efficiency are irrelevant to the best performance that can be obtained. Of course a considerable literature addresses the extension of thermodynamics to irreversible processes.⁵⁻⁹ Again it may be questioned whether this is adequate. Standard irreversible thermodynamics is linear,^{7,8,10} although few chemical reactions are operated in the linear region.^{11,12} Outside the linear region elementary thermodynamic quantities such as temperature and entropy may not be well-defined, or may be subject to somewhat arbitrary definition.¹³⁻¹⁷ Tykodi¹⁸ has discussed an

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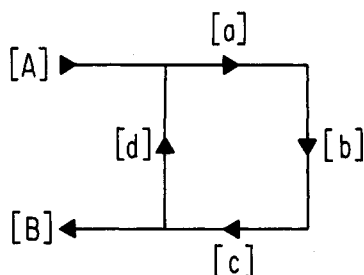


Figure 1. Schematic of process for fuel synthesis.

example of the limitations of linear irreversible theory, the Joule-Thomson porous plug experiment. Irreversible processes taking place at the plug might involve violent temperature and pressure variations, shock waves, pulsing, chemical reactions, all dependent on the physical characteristics of the gas and the plug, and all expected to be nonlinear. However, Jaynes¹⁹ points out "By a simple argument given in all the textbooks, we are persuaded at once that, however violent the irreversible processes taking place in the plug, ...when a steady state is reached, the (enthalpy + kinetic energy of mass flow) of the incoming and outgoing gases must be the same. In other words, established equilibrium theory does enable us to draw rigorous inferences about steady processes that begin and end in states of complete thermal equilibrium."

Now this is precisely what is needed in order to evaluate fuel synthesis scenarios, as our primary interest is not the temporal development of linear irreversible models; we merely wish to know the process efficiency, given the initial and final equilibrium states. The viewpoint of standard Gibbsian thermodynamics, with its emphasis on state functions,^{20,21} does not provide a satisfactory approach to this problem because the process variables of work and heat, which are path functions, are fundamentally more important for efficiency analysis than the state variables. However, with a reorientation so small as to appear almost insignificant, traditional thermodynamics can be expressed in a form that not only retains the rigor of established equilibrium theory, but also is completely adequate for irreversible processes that begin and end in equilibrium states. A key step in this reorientation was presented many years ago in a review article by Tolman and Fine.²² They showed that in order to describe irreversible processes with thermodynamics, one need only (1) write both the first and second laws as equalities, and then (2) explicitly evaluate the entropy produced by each irreversible source in the system.

For many chemical systems it is a simple matter to account for the major sources of entropy. In principle one can always follow the prescription of thermodynamics: construct a reversible path between the initial and final states of the system, and then use $\Delta S_{\text{irr}} = \int dq_{\text{rev}}/T$. In practice even this is seldom necessary, because the irreversible entropy produced in many elementary processes is already well-known in thermodynamics. Insofar as a given process can be described in terms of a few simple processes such as heat and mass transfer and chemical reactions, application of the present approach is straightforward.

In the next section we apply the program of Tolman and Fine to the problem of fuel synthesis. In this way we obtain an equality relation for the efficiency of any such process. The processes in mind are the production of simple fuels like hydrogen or methane from, say, solar energy and electricity; in the following sections

we show how the efficiency equation may be applied to the analysis of a few elementary processes of current interest.

II. The Efficiency of Fuel Synthesis

The skeleton of the thermodynamic process for fuel synthesis is diagrammed in Figure 1. At point [A] the reactants are inserted into the production line, carried through a series of processes [a], [b], and [c], where heat or solar energy is added, electrical and other sorts of work are done, etc., until at point [B] the products, including the fuel, are removed. Step [d] restores the system to the initial state to begin a new cycle. The boundaries of the system are chosen to include steps [a] through [d] so that, per cycle, there is a net input of reactants, work, and heat and a net output of products. We further stipulate that the boundaries are so drawn that except for heat transfer to or from the surroundings all entropy production occurs within the system.

The first law of thermodynamics may be written²²

$$\Delta E_{\text{sys}} = \sum E_m + \sum Q_n + w_{\text{tot}} \quad (1)$$

The first term on the right-hand side of eq 1 accounts for the energy change of the system due to the exchange of matter with the surroundings. The second term accounts for heat added to or rejected by the system, and the final term includes work done on or by the system.

For one complete cycle the system returns to the initial state, so that the change in energy must be zero:

$$\sum E_m + \sum Q_n + w_{\text{tot}} = 0 \quad (2)$$

Furthermore, the only matter added to the system is the reactants, and the only matter leaving the system is the products. Thus we may write

$$\sum E_m = -\Delta E_f \quad (3)$$

where ΔE_f is the energy that must be added to the reactants in order to convert them to the fuel and other products. The minus sign arises in eq 3 because by convention the thermodynamic energy difference is defined as $E_{\text{final}} - E_{\text{initial}}$, whereas the sum over E_m is for reactants minus products because reactants are added to the system and products are removed. Equations 2 and 3 give

$$\Delta E_f = \sum Q_n + w_{\text{tot}} \quad (4)$$

The second law of thermodynamics may be written²²

$$\Delta S_{\text{sys}} = \sum S_m + \sum (Q_n/T_n) + \Delta S_{\text{irr}} \quad (5)$$

The first term on the right-hand side accounts for the entropy carried by the flow of matter between the system and surroundings and is equal to the negative of the entropy difference between the products and reactants:

$$\sum S_m = -\Delta S_f \quad (6)$$

The second term on the right-hand side of eq 5 accounts for the change in entropy of the system due to the flow of heat between the system and the surroundings. The final term takes account of all irreversible sources of entropy production within the system.

Again, since the process is cyclic, ΔS_{sys} is zero and eq 5 becomes

$$\Delta S_f = \sum (Q_n/T_n) + \Delta S_{\text{irr}} \quad (7)$$

Equations 4 and 7 constitute a pair of simultaneous equations for the thermodynamics of the process, and they may be combined to eliminate any one of the Q_n . If the system includes heat transfer to many steps at different temperatures there will be only a small advantage in this. However, it is often possible to draw the boundaries so that the system has only a single internal heat reservoir. For example, one might consider solar heat at 6000 K to be the primary heat reservoir within the system. This reservoir is fed by the nuclear reaction outside the system. In a nuclear power plant the steam generators constitute a hot reservoir within the system at about 800 K, which is again fed by nuclear reactions outside the system. We assume, then, without fear of eliminating very many processes, that the system includes a single primary heat reservoir, at temperature T_h . Furthermore, all heat

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rejected by the process goes into a reservoir at the ambient temperature T_0 . With these conditions we may eliminate the heat rejected to the sink by multiplying eq 7 by T_0 and subtracting from eq 4. This gives

$$\Delta E_f - T_0 \Delta S_f = Q_h(1 - T_0/T_h) + w_{\text{tot}} - T_0 \Delta S_{\text{irr}} \quad (8)$$

The work may be separated into the PV work associated with transforming the reactants into products, plus any additional work

$$w_{\text{tot}} = -P_0 \Delta V + w \quad (9)$$

Equation 8 becomes

$$\Delta G_f = (1 - T_0/T_h)Q_h + w - T_0 \Delta S_{\text{irr}} \quad (10)$$

where $\Delta G_f = \Delta E_f + P_0 \Delta V - T_0 \Delta S_f$ is the Gibbs free energy of formation of fuel at ambient conditions. It is also the change in the Gibbs availability of the matter transformed into fuel by the process.²⁴ Since ΔG_f is the maximum work in excess of pressure-volume work which can be delivered by the fuel upon transforming it back to the reactants, we define the efficiency in terms of it:

$$\epsilon = \frac{w_{\text{max}}}{Q_h + w} = \frac{\Delta G_f}{Q_h + w} \quad (11)$$

The denominator of eq 11 is the total energy input for the process: the heat drained from the hot reservoir plus the work done on the system. Equation 10 may be solved for $Q_h + w$:

$$Q_h + w = \frac{T_h}{T_h - T_0} \left[\Delta G_f - \frac{T_0}{T_h} w + T_0 \Delta S_{\text{irr}} \right] \quad (12)$$

The efficiency of fuel synthesis is then given by

$$\epsilon = \frac{\Delta G_f(1 - T_0/T_h)}{\Delta G_f - \frac{T_0}{T_h} w + T_0 \Delta S_{\text{irr}}} \quad (13)$$

For a process such as electrolysis where there is no heat reservoir and all energy is delivered by work, the efficiency reduces to

$$\epsilon = \frac{\Delta G_f}{\Delta G_f + T_0 \Delta S_{\text{irr}}} \quad (14)$$

Equation 13 gives the efficiency of fuel synthesis in terms of the temperatures of the hot and cold reservoirs and the irreversible entropy produced within the system. One immediately recognizes the Carnot temperature factor $(1 - T_0/T_h)$ which gives the limiting efficiency should the process be carried out reversibly. For many cases, however, the Carnot limit is irrelevant to real performance. For example, with a solar temperature of 6000 K the Carnot factor is about 0.95, but it seems unlikely that any process could operate close to this efficiency. More important in practical circumstances is the role played by the entropy production. Because ΔS_{irr} must be positive it serves always to lower the efficiency.

In order to evaluate the entropy production for any given step of the process it is necessary to construct an ideal reversible path between the initial and final states, and then compute $\int dq_{\text{rev}}/T$. In practice this has already been done for the most commonly encountered simple processes. We list here the well-known expressions for a few processes that will be encountered below. Expressions for entropy production in many other processes may be found in the literature.²³⁻²⁷

Isothermal chemical reaction:

$$\Delta S_{\text{irr}} = -\Delta G/T \quad (15)$$

Heat transfer from T_h to T_c :

$$\Delta S_{\text{irr}} = \int_{T_{h1}}^{T_{h2}} C_h \frac{dT_h}{T_h} + \int_{T_{c1}}^{T_{c2}} C_c \frac{dT_c}{T_c} \quad (16)$$

Electric resistance in a circuit with current I flowing for time t :

$$\Delta S_{\text{irr}} = I^2 R t / T \quad (17)$$

A considerable number of fuel synthesis scenarios may be described in terms of these few sources of entropy production. Before proceeding to applications of the efficiency equation, it is convenient first to redraw the boundaries of the thermodynamic system. Section III is devoted to this topic.

III. High-Temperature Reservoir

It was pointed out in section II that the Carnot factor is of limited utility because often it has only a minor influence in the efficiency equation. Many processes employ a secondary heat reservoir or involve a high-temperature step at a lower temperature than the primary heat reservoir. For example, in thermochemical synthesis it would be convenient to regard the highest temperature reaction as a secondary heat reservoir. In practice it is unlikely that the system would be configured so that all heat is transmitted through one reactor, but since entropy is a state function dependent only upon the end points of a process, we may, without approximation, introduce the convenient fiction that all heat energy is delivered to the system by first going into the highest temperature stage, and from there to any other step which drains heat. The introduction of the fictitious intermediate step in the heat transfer does not alter the entropy. We may then redraw the boundaries of the system so that the primary heat reservoir is placed outside the system. Let T_p be the temperature of the primary reservoir and T_h the temperature of the secondary reservoir. Suppose also that there is a heat leak during the transfer from T_p to T_h , and let α be the fraction of heat lost to the surroundings at T_0 in this manner. The heat lost is αQ_p and the heat delivered is $(1 - \alpha)Q_p$, where Q_p is the heat drained from the primary reservoir. The total irreversible entropy is found by applying eq 16

$$\Delta S_{\text{tot}} = Q_p(1 - \alpha) \left(\frac{1}{T_h} - \frac{1}{T_p} \right) + \alpha Q_p \left(\frac{1}{T_0} - \frac{1}{T_p} \right) + \Delta S_{\text{irr}} \quad (18)$$

The first term on the right-hand side of eq 18 gives the entropy generated by the irreversible heat transfer from T_p to T_h . The second term is the entropy due to the heat leak, and the final term accounts for entropy generation within the new system boundaries. Equation 18 may be combined with the relations of section II to eliminate T_p in favor of α and T_h . The result is

$$\epsilon = \frac{\epsilon_p \Delta G_f(1 - T_0/T_h)}{\Delta G_f - \epsilon_p \frac{T_0}{T_h} w - (1 - \epsilon_p)w + T_0 \Delta S_{\text{irr}}} \quad (19)$$

where $\epsilon_p \equiv 1 - \alpha$ is the efficiency of the primary-to-secondary heat transfer. Equation 19 marks the difference between the present approach and a number of previous approaches. For example, Landsberg and Tonge^{28,29} give inequalities for the efficiency based upon the entropy decrease of the primary reservoir. This decrease is necessarily less than the entropy increase in the system due to the absorption of heat, and the Carnot factor of eq 19, which accounts for this, is a better estimate of the efficiency.

We proceed now to applications of the efficiency equation to some illustrative processes of current interest. It is not our purpose to carry out an exhaustive investigation of any single process, as it will soon be evident that a large number of engineering details must be accounted for before this can be done. Rather our approach is more in the spirit of section I; we wish to provide a

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reasonably simple method for efficiency evaluation. This is achieved by accounting for the major entropy generating steps of the process.

IV. Thermochemistry

It is not possible by any sequence of chemical reactions to synthesize the fuel while operating solely at the temperature of the cold reservoir, no matter how much heat is supplied. Equation 19 contains this information, somewhat redundantly, in two places. The Carnot factor and therefore the efficiency would be zero for such a process. Also the entropy of reaction would be, from eq 15

$$\Delta S_{\text{irr}} = -\sum \frac{\Delta G_i}{T_i} = -\frac{1}{T_0} \sum \Delta G_i = \frac{-\Delta G_f}{T_0} \quad (20)$$

Since energy is stored in the fuel, ΔG_f is positive. As this gives a negative value for ΔS_{irr} , the process cannot occur spontaneously.

There are two ways to overcome this restriction. If ΔS_f is positive, ΔG_f becomes negative at sufficiently high temperature, and under these conditions the reaction becomes spontaneous. Another approach, which is the only thermochemical method possible if ΔS_f is negative, is to carry out a sequence of reactions at different temperatures so that the T_i cannot be extracted from the sum in eq 20, in which case the entropy may again be positive. Our first fuel synthesis process, high-temperature direct splitting of water, employs the former approach.

Several research groups have built small-scale solar reactors for hydrogen production by one-step water decomposition at high temperature.³⁰⁻³² At 2500 K water is split to 4% mole fraction of H_2 .³³ The entropy of reaction, from eq 15, is given by

$$\Delta S_{\text{irr}} = -\frac{1}{T_h} \left[\Delta G^\circ + RT_h \ln \frac{[\text{H}_2\text{O}][\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]} \right] \quad (21)$$

Equation 21 gives 4.35 cal/(mol of H_2 deg) for the entropy at 2500 K. If this were the only source of entropy the process would be very efficient. However, the hydrogen has not been separated from the reaction mixture, and materials limitations prevent high-temperature separation.³⁵⁻³⁷ An alternative to high-temperature separation is to quench the mixture so rapidly that the back reaction is stopped, and then separate the hydrogen at low temperature.³⁸⁻⁴⁰ We now use the quenching strategy to close the cycle by accounting for the entropy with eq 16. The entropy of heating the water to T_h is

$$\Delta S_{\text{irr}} = N \left[C_l \ln \frac{T_b}{T_0} + \frac{\Delta H_v}{T_b} + C_g \ln \frac{T_h}{T_b} \right] - \frac{N}{T_h} [C_l(T_b - T_0) + \Delta H_v + C_g(T_h - T_b)] \quad (22)$$

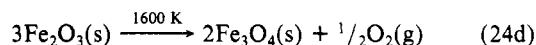
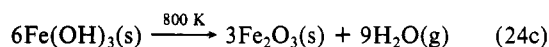
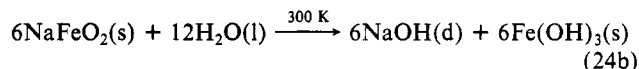
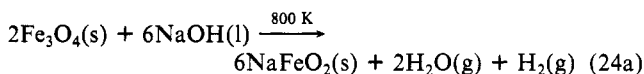
The first bracket encloses the entropy change of the water, and the second bracket encloses the entropy loss of the virtual hot reservoir. C_l is the heat capacity of the liquid, C_g is the heat capacity of the gas at constant pressure, and ΔH_v is the enthalpy

of vaporization at boiling point T_b . N is the number of moles of water needed to deliver 1 mol of hydrogen, 24.5 at 2500 K. The entropy of quenching the sample to room temperature is

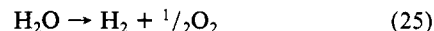
$$\Delta S_{\text{irr}} = \left[(C_{\text{H}_2} + C_{\text{O}_2}/2) \ln \frac{T_0}{T_h} + (N-1) \times \left(C_l \ln \frac{T_0}{T_b} + C_g \ln \frac{T_b}{T_h} - \frac{\Delta H_v}{T_b} \right) \right] + \frac{1}{T_0} [(C_{\text{H}_2} + C_{\text{O}_2}/2)(T_h - T_0) + (N-1)(C_l(T_b - T_0) + C_g(T_h - T_b) + \Delta H_v)] \quad (23)$$

The first bracket here encloses the entropy change of the effluent, and the second bracket encloses the entropy increase of the surroundings due to the transfer of heat. The total entropy produced in the cycle is 2.51 kcal/(mol of H_2 deg). We have recently completed kinetic studies of injection quenching of the effluent from the direct splitting reactor and found that only 76% of the hydrogen is recovered.⁴⁰ This increases the generated entropy per mole of H_2 recovered to 3.30 kcal/(mol deg). The efficiency factor ϵ_p is determined by reflection losses in the collectors and radiation by the reactor and has been estimated to be 0.70.⁴¹ The thermochemical ϵ_p losses appear to be sensitive to engineering details such as coatings and insulation, and so we will not analyze them in detail, but simply take values suggested by others. The losses could be widely variable, and as large as 70% for some collector designs. At room temperature ΔG_f is 57.8 kcal/(mol of H_2).³⁴ Inserting the above into eq 19 gives an efficiency of 0.032.

The simple direct-splitting reactor, with two heat transfers, one chemical reaction, and a heat leak from the primary reservoir, contains most of the features of more complex thermochemical fuel synthesis. Multistep thermochemical cycles for hydrogen synthesis have received much attention in recent years.^{1-4,42-45} Bamberger and Richardson⁴⁶ have discussed the following example, which has been demonstrated in the laboratory.



This sequence of reactions is fairly typical of thermochemical cycles. There are two low-temperature heat injection steps, (24a) and (24b), and two high-temperature heat absorption steps, (24c) and (24d). The net reaction for a full cycle is the same as for direct splitting:



Several authors have investigated the efficiency of thermochemical cycles, and it has been recognized for a number of years that the Carnot limit applies.^{44,45,47,48} Again, though, it is not expected that the process may operate close to this limit. In the remainder of this section we will employ the Bamberger-Richardson cycle as a guide in the identification of the main sources of entropy in thermochemical fuel synthesis. In order to maintain a simple notation we assume that the heat capacities are constant. Furthermore, we assume that the heat capacities have been multiplied

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by the stoichiometric coefficients of the reaction sequence, so that mole number symbols are suppressed.

A first source of entropy arises from heat transfer to the reactions at intermediate temperatures, (24a) and (24c). The entropy change is

$$\Delta S_{\text{irr}} = \sum_i \Delta H_i \left(\frac{1}{T_i} - \frac{1}{T_R} \right) \quad (26)$$

for reaction temperature T_i and virtual reservoir temperature T_R . For endothermic reactions T_R is T_h , and for exothermic reactions T_R is T_0 . Since the high-temperature reaction is endothermic, and the low-temperature reaction is exothermic, eq 26 applies to all of the reactions. This source of entropy may be coupled to the heat exchange strategy below, but in the present case reaction 24a rejects only 4.11 kcal, and there is little advantage in recovering this heat. Equation 26 may be combined with the entropy of reaction, $-\Delta G_i/T_i$, to give

$$\Delta S_{\text{irr}} = \sum_i \Delta S_i - \Delta H_i/T_R \quad (27)$$

where the sum is over all reactions i .

A major source of heat-transfer entropy arises from the need to restore the products to the reactant temperatures in order to close the thermodynamic cycle. Each species, except for those of reaction 25, is a reactant at one temperature and a product at another temperature. The chemical processing industry employs two types of heat exchangers for internal energy recovery—direct contact and countercurrent.^{49,50} Since in the present case most of the species are solids, it is necessary to employ direct contact recuperators. In practice there is little difference between direct contact and countercurrent heat recovery when the two substances have significantly different heat capacities. This is true in the present case where heating of the $\text{Fe}(\text{OH})_3$ from 300 to 800 K takes up most of the heat of the substances which are cooled.

The entropy generated in a heat exchange between two substances A and B is

$$\Delta S_{\text{irr}} = C_A \ln \frac{T_{\text{he},A}}{T_{p,A}} + C_B \ln \frac{T_{\text{he},B}}{T_{p,B}} \quad (28)$$

$T_{p,i}$ is the temperature at which the substance is a product species, and $T_{\text{he},i}$ is the temperature achieved in the heat exchanger. For direct contact heat exchange the first law heat balance gives the following expression for the final temperatures:

$$T_{\text{he},A} = T_{\text{he},B} = \frac{T_{p,B} + \left(\frac{C_A}{C_B} \right) T_{p,A}}{1 + C_A/C_B} \quad (29)$$

From the temperatures achieved in the heat exchangers each species must be heated or cooled by the virtual reservoirs to the reactant temperatures of eq 24 in order to close the cycle. The entropy generated in the heat restoration of the cycle is

$$\Delta S_{\text{irr}} = \sum_A C_A \ln (T_i/T_{\text{he}}) - C_A(T_i - T_{\text{he}})/T_R \quad (30)$$

where T_i is the reactant temperature of species A and T_R is the virtual reservoir temperature, T_h for substances to be heated, and T_0 for substances to be cooled. The entropy of eq 27–30 may be combined in various ways to obtain a simpler expression, if we invoke the condition that all species except those of reaction 25 are cycled. We may employ the following relations:

$$\sum_i \Delta H_i(T_0) = \Delta H_f \quad (31)$$

$$\sum_i \Delta S_i(T_0) = \Delta S_f \quad (32)$$

$$H_A(T_i) = H_A(T_0) + C_A(T_i - T_0) \quad (33)$$

$$S_A(T_i) = S_A(T_0) + C_A \ln (T_i/T_0) \quad (34)$$

$\Delta H_i(T_0)$ and $\Delta S_i(T_0)$ are the enthalpy and entropy of reaction at T_0 . Combining (27), (28), and (30) with the relations (31)–(34) gives the following expression:

$$\Delta G_f + T_0 \Delta S_{\text{irr}} = (1 - T_0/T_h) \sum_{\text{endo},i} \Delta H_i(T_0) - T_0 \sum_i \frac{(T_i - T_0) \Delta C_p}{T_{R,i}} - T_0 \sum_{\text{prod}} \frac{C_A(T_{i,A} - T_{\text{he},A})}{T_{R,A}} \quad (35)$$

The first sum of eq 35 is over the endothermic reactions. The second sum is over all reactions i ; $T_{R,i}$ is the temperature of the virtual reservoir drained by the reaction at temperature T_i , and ΔC_p is the heat capacity of the products minus the heat capacity of the reactants. The final sum is over all species which drain reservoir $T_{R,A}$ in the heat restoration of the cycle to the reaction temperatures $T_{i,A}$, after the heat exchange has brought the species to $T_{\text{he},A}$.

The products of reaction 24c are in different phases, so that no separation work is required. The other reactions require product separation, which contributes to w and ΔS_{irr} . The separation work and entropy may be found from eq 1 and 5 of section II. Since the matter flowing into the separator is the same as the matter flowing out, $\sum S_m$ and $\sum E_m$ are zero. We assume that the separation is isothermal and ideal so that ΔE is zero and ΔS is given by²⁵

$$\Delta S_{\text{sys}} = nR \sum x_i \ln x_i \quad (36)$$

where the x_i are mole fractions. The minimum work of separation is

$$w_{\text{rev}} = \Delta G = -T \Delta S_{\text{sys}} \quad (37)$$

We introduce an efficiency factor ϵ_s so that the actual work is

$$w = \frac{w_{\text{rev}}}{\epsilon_s} = -\frac{T \Delta S_{\text{sys}}}{\epsilon_s} \quad (38)$$

The efficiency factor depends on the pumps and other devices employed for the separation. For membrane separation ϵ_s may be thought of as the partial pressure ratio developed across the membrane and pumps. We do not wish to analyze the thermodynamics of separation devices here, so below it will be assumed that ϵ_s is 0.5. Finally, we assume that the separation is carried out with no heat drain from the hot reservoir, $Q_h = 0$. Substituting the above into eq 1 and 5 gives $Q_0 = -w$ and

$$\Delta S_{\text{irr}} = \Delta S_{\text{sys}} + \frac{w}{T_0} \quad (39)$$

The entropy and work terms of the efficiency equations are then given by

$$-(\epsilon_p(T_0/T_h - 1) + 1)w + T_0 \Delta S_{\text{irr}} = \Delta S_{\text{sys}} \left[T_0 + T \frac{\epsilon_p}{\epsilon_s} \left(\frac{T_0}{T_h} - 1 \right) \right] \quad (40)$$

Finally, reactions 24a, 24b, and 24d generate entropy of mixing, given by the negative of eq 36.

Tables I and II give the results of applying the above to the Bamberger–Richardson Cycle. Table I presents a simple direct-contact heat exchange strategy, and also gives the entropy generated in heat restoration of the cycle. We have examined alternate heat exchange strategies and found entropies larger by 5–20%. Little heat is recovered from the H_2 and O_2 due to their low heat capacities, and an engineer would probably disdain trying to recover heat from them; in any event this has only a small effect on the entropy. Table II lists all losses and sources of entropy described above. The ϵ_p factor is only a guess, based upon a minimum loss of about 9% for the collectors.⁵¹ Reaction 24d

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TABLE I: Entropy and Temperatures (Kelvin) for Heat Exchange Strategy and Heat Restoration of Cycle for Reactions 24

Heat Exchange						
substance heated	T_p	T_{he}	substance cooled	T_p	T_{he}	ΔS , cal/(mol deg)
Fe ₂ O ₃	800	1186	Fe ₃ O ₄	1600	1188	8.68
Fe(OH) ₃	300	517	Fe ₃ O ₄	1186	800	40.7
NaOH	300	516	NaFeO ₂	800	516	21.1
Fe(OH) ₃	517	637	H ₂ O	800	637	5.22
Fe(OH) ₃	637	646	H ₂	800	646	0.27
Fe(OH) ₃	646	677	O ₂	1600	677	2.24
NaOH	516	579	H ₂ O	637	579	1.00
NaOH	579	584	H ₂	646	584	0.03
NaOH	584	588	O ₂	677	588	0.05

Final Heating and Cooling			
substance	T_{he}	T_f	ΔS , cal/(mol deg)
Fe ₂ O ₃	1186	1600	3.09
NaOH	588	800	7.69
Fe(OH) ₃	677	800	11.3
Fe ₃ O ₄	800	800	0
NaFeO ₂	516	300	12.8
H ₂ O	579	300	97.6
O ₂	588	300	1.22
H ₂	584	300	1.96

TABLE II: Losses and Entropy Contributions for the Bamberger-Richardson Thermochemical Cycle

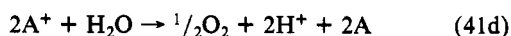
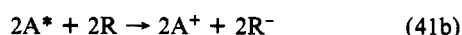
loss or entropy term	eq	this cycle
heat leak factor ϵ_p		0.85(?)
entropy of reaction, cal/(mol deg)	15	295
entropy of heat exchange and heat recuperation, cal/(mol deg)	28, 29	215
entropy of heat transfer to intermed temp reactions, cal/(mol deg)	26	54.4
separation, kcal/mol	40	12.1
entropy of mixing, cal/(mol deg)	36	41.1
Carnot factor		0.85
efficiency	19	0.16

has a positive free energy change as written and so is not spontaneous. In ref 46 the oxygen was removed continuously by sweeping the reactor with argon. For Table II we have assumed this approach, and that the mole fraction of oxygen in the argon has been brought to the equilibrium value of 0.063. The overall efficiency of the Bamberger-Richardson cycle is estimated to be 0.16.

It is clear from this example that, while certain engineering features must be specified, the major contributions to the entropy production in thermochemical fuel synthesis are easily determined with the help of eq 15, 16, and 40. No original thermodynamics is necessary. In the next section we discuss systems which are not so easily handled with traditional thermodynamics.

V. Photochemistry

Grätzel has recently discussed photochemical fuel synthesis processes of the following type^{52,53}



In the usual vocabulary A is the sensitizer, with excited state A*, and R is the relay. Note that $h\nu$ is not included explicitly as a

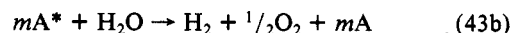
reactant in (41a), only implicitly as if it were heat. Although the details of the reactions vary from case to case, the general scheme of excitation and energy transfer to a receptor followed by a sequence of chemical reactions is usually retained. Previous approaches to the thermodynamics of photochemical fuel synthesis have treated the problem as a sequence of chemical reactions by assigning different chemical potentials to the species A and A*.⁵⁴⁻⁶⁰ On first sight it would appear that this approach must fail, since we know from section IV that no fuel can be produced in an isothermal sequence of chemical reactions. An additional difficulty, mostly formal, is that excited species, like photons, are not conserved in particle number, so that their chemical potentials are zero.⁶¹ At the end of this section we will show the difference between the present approach and the more common chemical potential formalism.

A high-temperature step may be introduced into the system, and chemical potentials avoided, by treating (41a) as an effect on the population distribution or as populating a reservoir, rather than as a reaction. The temperature of the hot reservoir is then given by

$$\frac{n_{A^*}}{n_A} = \frac{g_{A^*}}{g_A} e^{-h\nu_0/kT^*} \quad (42)$$

A number of authors have discussed how a consistent thermodynamics may be based on temperatures defined through populations.⁶²⁻⁶⁹ The present case is only slightly different, as the system is now characterized by two simultaneous temperatures, $T_h \equiv T^*$ and T_0 . The entropy generated in the system by (41a) is $N_0 h\nu_0/T^*$, where N_0 is Avogadro's number. This entropy is already included in eq 19 through the Carnot factor, so (41a) is not to be included when ΔS_{irr} is computed. The advantage of drawing the system boundary to include only the excited states is that we do not need to consider the entropy of the radiation, which lies outside the system by virtue of the transformation of section III.

Suppose now that we have an arbitrarily long sequence of chemical reactions, but the net reaction, when they are added together, is to split water:



Here m is the stoichiometric requirement of excited species. The boundary of the system is drawn to include only effective water-splitting reactions. Side reactions are placed outside the system, as will be discussed below. The entropy due to (43a) is accounted for with the Carnot factor, and ΔS_{irr} is due to (43b) alone. Reaction 43b is the sum of two reactions, so ΔS_{irr} is given by

$$\begin{aligned} \Delta S_{irr} &= \frac{-\Delta G_f}{T_0} - \Delta G(mA^* \rightarrow mA)/T_0 \\ &= [mN_0 h\nu_0(1 - T_0/T^*) - \Delta G_f]/T_0 \end{aligned} \quad (44)$$

Thus no matter how long the sequence of reactions, the entropy

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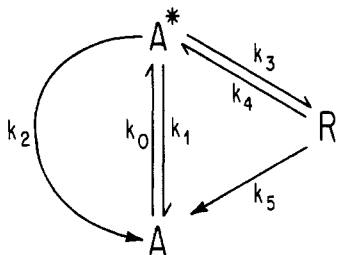


Figure 2. Model for photochemical energy storage.

is easily evaluated if T^* is known. In this section we concentrate on finding T^* and the direct losses ϵ_p . We note, however, that if the stoichiometric requirement m is known, T^* is not needed to find the efficiency, since eq 19 reduces upon substitution of eq 44 to

$$\epsilon = \epsilon_p \Delta G_f / m N_0 h \nu_0 \quad (45)$$

The radiation temperature T^* does not affect the efficiency of the process, only the spontaneity through the requirement that ΔS_{irr} of eq 44 be positive.

Our model for photochemical energy storage is diagrammed in Figure 2. The rate constants k_0 and k_1 account for absorption and emission of radiation in the presence of the electromagnetic field. The excited-state energy is passed to the relay and stored with rate constant k_3 . We allow this process to be reversible by including k_4 . The excited species returns to the ground state with rate constant k_5 . The constant k_2 is the sum of rate constants for all competing side reactions which do not result in energy storage, such as thermal and nonradiative decay of the excited state or of any charge-transfer species produced from it. In the steady state the reaction sequence of Figure 2 gives the concentrations in the relation

$$\frac{A^*}{A} = \frac{k_0}{k_1 + k_2 + k_R} \quad (46)$$

where $k_R = k_3 k_5 / (k_4 + k_5)$.

The rate constants k_0 and k_1 may be expressed in terms of the Einstein absorption and emission coefficients.^{70,71} We are concerned here with condensed-phase spectra for which the Einstein model does not strictly apply, but the corrections remain controversial, and we will not use them.^{72,73} In practice it is often easiest to write the rate constants in terms of the maximum of the (log) absorption coefficient, ϵ_{max} . Assuming that the band profile is Lorentzian⁷⁴ and that the radiation energy density is roughly constant over the band, one obtains

$$k_1 = 9.048 \times 10^{12} \gamma \epsilon_{\text{max}} / \lambda_0^4 \quad (47)$$

$$k_0 = k_1 \alpha / (e^{h\nu_0/kT} - 1) \quad (48)$$

In eq 47 ϵ_{max} is in liter/(mol cm), and γ and λ_0 are in nanometers; γ is the half-width at half-height. The exponential factor in eq 48 arises from an assumed Planck distribution law for the energy density of the electromagnetic field.⁷⁵ Below we will use 6000 K for the solar temperature in eq 48.^{76,77} The parameter α in eq 48 accounts for the drop in intensity due to distance from the source, clouds, etc. The value of α obtained from the solar constant is 4.95×10^{-6} . This does not include losses due to atmosphere and source inclination. The average daylight July surface radiation flux at 30° N latitude gives $\alpha = 2.14 \times 10^{-6}$.⁷⁸ The latter value will be employed below. If the radiation is focused, α is simply multiplied by the concentration factor.

The direct losses ϵ_p in photochemistry have received much attention, but we discuss them briefly for completeness and because the present approach may be employed to improve their estimation. The common separation of the ϵ_p factor is to write it as the product: (fraction of energy captured) \times (fraction of captured energy used in reaction). The first factor is usually written^{79,80}

$$\eta_1 = \frac{h\nu_0 \int_0^\lambda I(\lambda) d\lambda}{\int_0^\infty I(\lambda) hc / \lambda d\lambda} \quad (49)$$

where I is the radiation intensity. For the widely investigated Ru(bpy)₃²⁺ sensitizer,⁸¹⁻⁹⁰ η_1 is 0.20.⁸⁰ For chlorophyll η_1 is 0.35, and for bacteriochlorophyll it takes on a maximum value of 0.44.⁵⁶ Equation 49 incorporates the Shockley-Queisser condition that all light at frequencies above ν_0 is absorbed.⁹² This overestimates the efficiency by at least a few percent, and much more for narrow bands, but allows the sample depth to be removed from the problem. It is shown in the Appendix how much more accurate η_1 efficiencies may be determined.

The second efficiency factor is the quantum yield. For the reaction model of Figure 2 the fraction of absorbed energy directed into the fuel-producing reactions is

$$\eta_2 = \frac{k_R}{k_1 + k_2 + k_R} \quad (50)$$

The overall efficiency may now be written

$$\epsilon = \eta_1 \left(\frac{k_R}{k_1 + k_2 + k_R} \right) \frac{\Delta G_f}{m N_0 h \nu_0} \quad (51)$$

Further reduction of this expression is hampered because at the present time there is no general theory which permits evaluation of the rate of nonradiative decay. Side reactions are difficult or impossible to predict. The sum of rate constants k_2 must be treated as an empirical parameter. A small reduction of eq 51 is possible in one situation. Many times the predominant mechanism for nonradiative decay in solution is quenching due to dimers.⁹³⁻⁹⁵ Consider the case where this is the only mechanism for nonradiative decay, and assume for simplicity that pair formation, whether it be absorber-absorber (AA) or absorber-receptor (AR), has no effect on the transition dipole moment, so that pairs decay to energy loss (AA) or energy storage (AR) at the same rate as monomers. Here a pair may be considered to be two species lying within the diffusion length for the excited-state lifetime. Then $k_2/k_R = P_{AA}/P_{AR}$ and $k_1/k_2 = P_A/P_{AA}$, where P represents the probability of finding one of the species. If there is no specific

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bond between A and R, P_{AR} will be small in dilute solution and η_2 reduces to P_{AR}/P_A , which is some small fraction of the receptor mole fraction. This merely indicates that it is desirable to have a large excess of receptors or, better, to have the absorber bonded to the receptor. Additionally, it may be permissible in some situations to neglect the k_2 losses.

We now investigate the scheme of reactions 41 assuming that the sensitizer is $\text{Ru}(\text{bpy})_3^{2+}$ and that k_2 is zero. The quantum energy is 47.8 kcal/mol and the partial efficiency $\eta_1 \Delta G_f / mN_0 h\nu_0$ is 0.11. This is the base efficiency which cannot be exceeded, and we wish to know how the requirement of spontaneity will affect k_R and η_2 . The absorption coefficient is $14\,500 \text{ L mol}^{-1} \text{ cm}^{-1}$,⁸⁰ which gives $k_1 = 9.6 \times 10^7 \text{ s}^{-1}$ and $k_0 = 3.76 \text{ s}^{-1}$ at unit solar intensity. So long as k_R exceeds 10^9 s^{-1} the η_2 efficiency will be better than 90%. By substituting the radiation temperature from eq 42 into the entropy equation (44) one obtains the following bound on k_R :

$$mN_0 h\nu_0 + mRT_0 \ln \frac{k_0}{k_1 + k_R} - \Delta G_f > 0 \quad (52)$$

Equation 52 gives $k_R < 2.5 \times 10^{15} \text{ s}^{-1}$, which allows considerable freedom for a high η_2 efficiency. As the rate k_R increases, the irreversible entropy of reaction decreases, providing a simple example of a system which does not obey the assumptions of the Onsager theory.⁹⁶⁻⁹⁸

It is not only required that the total entropy be positive, but that the entropy produced in each step be so. Although we do not know the free energy changes for most of the steps, reaction 41e is easily taken into account. The free energy change is $\Delta G_e = \Delta G^\circ_e - RT_0 \ln [H^+][OH^-]$, where ΔG°_e is -19.3 kcal/mol .⁹⁹ In the steady state the rate of energy conversion is equal to the rate of reaction 41e

$$k_R[A^*] = \frac{k_R k_0[A]}{k_1 + k_R} = \frac{k_e}{2} [H^+][OH^-] \quad (53)$$

where k_e is $1.4 \times 10^{11} \text{ s}^{-1} \text{ M}^{-1}$.¹⁰⁰ Combining the above gives

$$2RT_0 \ln \frac{k_e}{2k_R[A]} > \Delta G_f - 2\Delta G^\circ_e - 2N_0 h\nu_0 \quad (54)$$

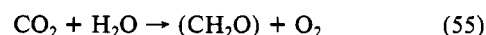
or $k_R[A] < 5 \times 10^{11} \text{ M s}^{-1}$. Although it is of interest that there exists an upper bound on the absorber concentration beyond which the steady state cannot be maintained, this is not a strong bound since $[A]$ could be as large as 10–20 M while the η_2 efficiency remains close to unity. Thus with the limited information available we have not found any condition which might affect the spontaneity or put significant bounds on the η_2 efficiency. A more effective application will require knowledge of the free energy changes and rates for more of the reactions, and this information is currently unavailable.

We now explain the difference between the photochemical thermodynamics presented here and the chemical potential approach.⁵⁴⁻⁶⁰ A formal similarity between the two may be established through the relation $\Delta\mu^* = \Delta E + RT_0 \ln A^*/A = N_0 h\nu_0 (1 - T_0/T^*)$, where $\Delta\mu^*$ is the excess chemical potential of the excited state over the ground state. (Note that if one uses T^* in the definition of $\Delta\mu^*$, the chemical potential is zero.) This relation identifies the chemical potential as a Carnot limit for energy storage, which would be realized should the process occur reversibly. As shown above, however, once the entropy of reaction has been taken into account, the efficiency no longer depends upon T^* . This is because a process spontaneous at some value of T^* or $\Delta\mu^*$ remains spontaneous at any higher value of these quantities, while the efficiency depends only on the free energy ΔG_f stored

in the product. This appears to be different from the conclusions of ref 59. But fundamentally T^* is employed here only as an intermediate quantity which facilitates the determination of ΔS_{irr} and the efficiency. The range of validity of eq 44 as a predictor of spontaneity may be questioned. In kinetic theory the rate constant for reaction includes an exponential factor to account for the fraction of the Boltzmann population which exceeds the activation energy. Since the temperature T^* is associated with a narrow range of energy values for excited species this fraction is essentially either zero or one in photochemistry. In the former case eq 44 may predict spontaneity while the activation barrier prevents reaction. This might be rectified by replacing ΔG_f by the free energy of activation in eq 44. In any event, a positive ΔS_{irr} is a necessary but not sufficient condition for photoreaction.

VI. Biochemical Photosynthesis

In the previous section, the analysis could not be carried out completely because of lack of data; biochemical photosynthesis is well enough studied to serve as an example for the method of thermodynamic analysis we present here. The data crucial for this analysis are now summarized. Then we go on to evaluate the efficiency of photosynthesis with the performance of the Hill reaction as the index. The overall reaction in photosynthesis is



with a standard free energy change of 120 kcal/mol of O_2 .¹⁰¹ The quantum requirement is eight red photons of energy 42.3 kcal/mol.¹⁰² With an η_1 efficiency of 0.35 for absorption near 680 nm,⁵⁶ the partial efficiency $\eta_1 \Delta G_f / mN_0 h\nu_0$ is 0.12. Previous thermodynamic analyses of photosynthesis based on Carnot inequalities have given bounds far above this value.¹⁰³⁻¹¹³ The η_2 efficiency is variable because the photosystem saturates at low light intensity. We will discuss saturation below and for the moment assume that the light intensity is no greater than 10^{-3} sun (about $10^{-10} \text{ mol photons cm}^{-2} \text{ s}^{-1}$) and that the system is unsaturated. It is currently believed that there is negligible nonradiative decay in the chlorophyll antennae because the protein matrix prevents dimer formation^{114,115} so that energy is delivered to the trap by resonance transfer^{116,117} with a k_2 of zero (see Figure 2). The rate constant k_1 , from fluorescence lifetime measurements, is $6.67 \times 10^7 \text{ s}^{-1}$.^{101,118} The observed fraction of in vivo fluorescence extrapolated to zero incident intensity is 0.023.¹¹⁹ If this is set equal to $1 - \eta_2$, it corresponds to a $1/k_R$ value of 350 ps.¹²⁰ Both Mauzerall¹²¹ and Gulotty et al.¹²² have recently

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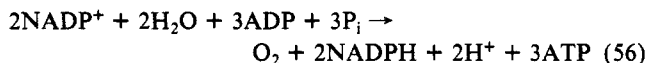
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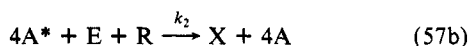
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observed fluorescence components in vivo with lifetimes in the 300–400-ps range. There is some uncertainty, but the interpretation we employ here is that the 350-ps component is due to decay of the trap through the electron transport chain, and we may employ this value for $1/k_R$ in the absence of saturation. From eq 42 and 46, the effective radiation temperature of the chlorophyll array at 10^{-3} sun is 787 K. From eq 44, the total irreversible entropy of reaction is 309 cal/(deg mol of O_2). Also of interest is the entropy generated by the light-induced reactions, without carbon fixation:



The standard free energy change for reaction 56 is about 142 kcal/mol of O_2 and could be lower by up to 13 kcal due to uncertainties in the in vivo phosphorylation free energy change.¹²³ Reaction 56 assumes that the carbon is fixed by the Calvin cycle.¹²⁴ The Hatch–Slack pathway would require an additional ATP, or 154 kcal.¹²⁵ Since in the Z scheme there is a phosphorylation along the electron transport pathway between PSII and PSI, four ATP may be produced stoichiometrically, even though only three are needed for carbon fixation, and so we use 154 kcal/mol of O_2 for the free energy change. The total irreversible entropy generated by the net light-induced reaction at 10^{-3} sun is 193 cal/(deg mol of O_2). The minimum quantum requirement for this reaction is six photons, and exceeds six photons if the light intensity is less than 2.7×10^{-4} sun. At less than 5.7×10^{-7} sun the quantum requirement exceeds seven photons, and at 5.8×10^{-9} sun ΔS_{irr} is zero for the light reactions.

We now discuss the estimation of η_2 . Some years ago Sauer and Park¹²⁶ found that the four-photon quantum requirement for the Hill reaction for the photoreduction of ferricyanide by chloroplasts is nearly doubled at 0.01 sun, but if the phosphorylation is decoupled with methylamine the quantum requirement becomes roughly independent of intensity at four photons. They concluded that there is a slow step associated with the phosphorylation such that the Hill reaction exhibits saturation at low light intensity. The kinetics of photosynthesis are undoubtedly very complex, but it is of interest to find the most elementary one-step saturation efficiency. This may be determined from the sequence



where A represents chlorophyll and E the species or enzyme which is saturated. It is assumed that the reactants R and products P are present in large excess and do not affect the kinetics. In the steady state the efficiency is found to be

$$\eta_2 = \frac{I_{1/2}}{2I(4\eta_0 - 2)} + \frac{1}{2} - \frac{1}{2} \left[\left(\frac{I_{1/2}}{I(4\eta_0 - 2)} + 1 \right)^2 - \frac{4\eta_0 I_{1/2}}{I(4\eta_0 - 2)} \right]^{1/2} \quad (58)$$

where η_0 is the limiting η_2 efficiency at zero incident intensity

$$\eta_0 = \frac{4k_2 E_0}{4k_2 E_0 + k_1} \quad (59)$$

and $I_{1/2}$ is the light intensity at which the efficiency is 0.5:

$$\frac{I_{1/2}}{I} = \left(\frac{4\eta_0 - 2}{\eta_0} \right) \left(\frac{4E_0 k_3}{A_0 k_0} \right) \quad (60)$$

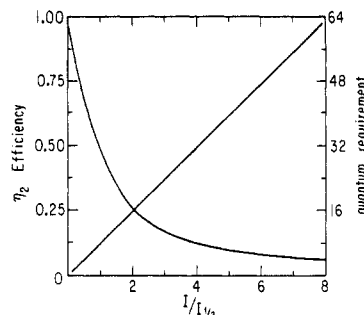


Figure 3. Efficiency and quantum requirement for one-step saturation of the Hill reaction as a function of the reduced intensity (eq 58).

A_0 and E_0 are the total amounts of chlorophyll and enzyme, respectively. The efficiency and quantum requirements for the Hill reaction are plotted in Figure 3. The curves have the same shape as those due to recent photoacoustic measurements by Carpentier et al.¹²⁷

In concluding this section we note that the unsaturated yield of photosynthesis exhibits a temperature dependence, with the efficiency dropping by as much as 30% for a 20-deg increase in temperature.¹²⁸ No temperature dependence has been included here because we employed the η_1 efficiency from eq 49. The revised model for the η_1 efficiency presented in the Appendix gives rise to a temperature dependence of the yield which is in the same direction as observed experimentally in photosynthesis. However, the analysis of this effect requires a much more detailed examination than may be presented here, and will be reported elsewhere.

VII. Electrochemistry

For electrolysis the efficiency is given by eq 14, and the entropy by eq 17. Suppose that the process is operated with constant current i for a time t needed to produce 1 mol of fuel. Then $it = nF$, where n is the number of electrons transferred and F is the Faraday constant. The voltage drop is¹²⁹

$$iR = V_{app} - V_{cell} = V_{app} - \Delta G_f/nF \quad (61)$$

where V_{app} is the applied voltage. The efficiency is then given by

$$\epsilon = \Delta G_f/nFV_{app} \quad (62)$$

Equation 62 is satisfactory for transient operation, but isothermal operation cannot be maintained at arbitrary voltage. The efficiency in a steady isothermal state may be found from eq 19. Although there is no high-temperature step, we may assume that the process is operated at a slightly elevated temperature, and then allow T_h to approach T_0 in the final step. The work is nFV_{app} and the entropy is

$$\Delta S_{irr} = [nFV_{app} - \Delta H_f + T_h \Delta S_f]/T_h \quad (63)$$

The Carnot factor of eq 19 is cancelled by another that arises in the denominator and the efficiency of the steady isothermal process is

$$\epsilon = \Delta G_f/\Delta H_f \quad (64)$$

For hydrogen electrolysis the efficiency is 0.83. If all the energy is supplied by electricity, the cell is said to be operated at the thermoneutral potential,¹³⁰ and no heat is exchanged with the surroundings. At voltages below $\Delta H_f/nF$ the cell cools and the heat must be added. If the voltage is greater than $\Delta H_f/nF$ then

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heat is rejected by the system and an additional contribution to the entropy must be included.

It is in a sense unsatisfactory to treat electricity and heat on an equal basis because the electricity is often obtained from another heat source. Fossil fuel plants deliver electricity at about 40% efficiency,^{131,132} and photovoltaic devices currently operate at about 11% efficiency.¹³³ Based upon this, Bockris¹³⁴ has suggested that some improvement might be had in electrolysis if the process were operated at high temperature, say 1000 °C. At high temperature the free energy of reaction is smaller and the electrical work needed for spontaneity is reduced. We may formulate this quantitatively by redrawing the boundaries of the system to include the cell and generator. The efficiency is $\Delta G_f / (Q_h + Q_e)$ where Q_h is the heat delivered to the cell, and Q_e is the heat delivered to the electrical generator. We may write $Q_e = w/\epsilon_e$, where ϵ_e is the efficiency of electricity generation. With the help of the relations from section II, the efficiency is found to be

$$\epsilon = \frac{(1 - T_0/T_h)\Delta G_f}{\Delta G_f + T_0\Delta S_{\text{irr}} + w \left[-1 + \frac{1}{\epsilon_e}(1 - T_0/T_h) \right]} \quad (65)$$

and the entropy includes all except that which is developed in the generator. In order to find the work and entropy for high-temperature thermal-assisted electrolysis, it is assumed below that the process is carried out at 0.1 V above the reversible potential at the operating temperature, to account for polarization effects.¹³⁴ Since the products are mixed with the reactants it is necessary also to include the entropy and work of separation. With the same approach as in section IV, the contribution to eq 65 due to separation is $\Delta S_{\text{sys}}[T_0 + (T_0 - T_h)/\epsilon_s\epsilon_e]$. The steady-state mole fractions of H_2 and O_2 must be known in order to find the separation entropy. At high product concentrations there may be kinetic losses in the cell due to side reactions. With the understanding that we have not investigated the possible kinetic losses, the results below are for 5% and 50% steady mole fraction of H_2 , with ϵ_e again taken to be 0.5.

A final source of entropy arises from heating the water to the operating temperature, and cooling the products to room temperature. Since the substances are fluids, a counterflow heat recuperator may be employed,⁵⁰ which can be operated with low entropy. The entropy is again given by eq 28 of section IV, but the first law heat balance is changed to

$$C_A(T_{\text{he,A}} - T_{i,A}) = C_B(T_{\text{he,B}} - T_{i,B}) \quad (66)$$

In counterflow heat recovery one may choose the temperature drop at one of the ports, say $(T_{\text{he,A}} - T_{i,B})$ at the high-temperature port, and then employ eq 66 to find the output temperature at the other port. For this case one of the ports was chosen to have a 10-deg temperature drop.³⁸ There is not enough heat in the products to raise the water through the phase transition and up to the operating temperature, so it was necessary to employ a three-stage heat exchange. In the first stage the products cool to 383 K while the steam heats to $T_h - 10$ K and a portion of the water vaporizes. In the second stage the remaining water vaporizes on contact with the hot reservoir. In the third stage the products cool to 310 K while the water heats from 300 to 373 K, first on contact with the products and then with the hot reservoir. Final temperatures of the reactants and products are adjusted to T_0 or T_h on contact with the cold or hot reservoirs, respectively.

Table III reports the efficiency of thermal-assisted electrolysis as a function of temperature for 40% and 11% electricity generation efficiency, assuming no heat leak from the reactor. Although the galvanic work is smaller at high temperature, the additional work and entropy of separation and heat transfer causes

TABLE III: Efficiency of Thermal-Assisted Electrolysis as a Function of Temperature^a

T, K	separated at 5% H_2		separated at 50% H_2	
	ϵ_1	ϵ_2	ϵ_1	ϵ_2
300	0.34	0.097	0.34	0.097
400	0.34	0.090	0.35	0.097
800	0.29	0.082	0.33	0.097
1200	0.26	0.075	0.32	0.095
1600	0.24	0.071	0.33	0.097

^a The ϵ_1 values assume that electricity is delivered at 40% efficiency, and the ϵ_2 assume it is delivered at 11% efficiency.

the efficiency to decrease as the temperature is raised. The results are more sensitive to the assumed efficiency ϵ_s than in the thermochemical case, but at least indicate that ϵ_s must be greater than 50% in order for the efficiency to be improved.

It is fitting that we conclude with the case of electrolysis, because it illustrates a certain hollowness in the present approach. It was not necessary to use the entropy to find eq 62 or 64, because they follow directly from the first law. In a similar way, the evaluation of the entropy production in photochemistry merely gave an efficiency factor $\Delta G_f/mN_0h\nu_0$, which again follows directly from the first law. In their treatment of viscous flow, Tolman and Fine state that "...in this case, we are led to the conclusion that the second law equality, although it gives us a valid expression, does not give us additional information beyond that already made available by the principles of mechanics and by the principle of conservation of energy generalized to allow for heat flow."²² In such cases, ΔS_{irr} does not provide original information, only a convenient bookkeeping scheme. This does not seem to be true in all cases; Bridgeman¹³⁵ has claimed that in the theory of the thermoelectric effect the entropy gives original information. For the fuel synthesis examples, losses due to mixing and separation appear to be treated more naturally and more easily with the second law rather than the first. The source of this apparent weakness of the Tolman-Fine approach may be traced to eq 5, where it is clear that we have invoked only the definition of the entropy, $\int dq_{\text{rev}}/T$, not the second law, $\Delta S_{\text{irr}} \geq 0$. For cases where the entropy is redundant for calculation of the efficiency eq 5 constitutes only a change in bookkeeping from heat to entropy; use of the definition of entropy is not by itself sufficient to obtain original information.

VIII. Conclusion

Although the processes discussed here operate far from the reversible limit, it is necessary to consider only a few sources of entropy in order to estimate the efficiency. These include entropy of reaction, of heat leak and heat transfer, and of voltage drop. Two important classes of fuel synthesis devices which have not been treated, the photoelectrochemical and photogalvanic devices,¹³⁶⁻¹⁴⁰ involve the same sources of entropy. We have examined only what might be called standard engineering configurations, such as isothermal chemical reactions and counterflow heat recuperators, which may not be optimal for energy efficiency. Recently the optimization of thermodynamic processes has attracted renewed attention,¹⁴¹⁻¹⁴⁷ and it is hoped that the present

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work provides a solid foundation for the thermodynamics of fuel synthesis which may serve as a basis for the consideration of more efficient design. In order to determine optimal designs it is necessary that all sources of entropy within the system be taken into account, or the results may be misleading. For example, if the entropy of reaction is neglected in photochemistry, the Carnot factor will appear to indicate that the efficiency may be improved by increasing T^* , while in fact T^* has no effect on the efficiency. In thermochemistry the entropy of reaction may be reduced to zero by following the equilibrium path of Gibbs theory. Again this may leave the efficiency unchanged, since the entropy of heat transfer from the reservoirs, eq 26, will increase. We have presented no rules whereby one may be assured that all sources of entropy have been taken into account, but the conditions that the cycle be closed and the products be delivered to ambient condition provides some guideline for the analysis. The present approach will still provide an upper bound on the efficiency when some entropy has been neglected, but optimization might simply give a larger bound unrelated to the actual performance.

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Appendix

The η_1 photochemical efficiencies that are given by eq 49 may be unrealistically large because it is assumed that all light above ν_0 is absorbed and utilized. More accurate expressions for η_1 are presented here.

As the radiation passes through the medium the intensity drops, which causes the radiation temperature of the sensitizer to decrease. At a certain depth, X_{\max} , T^* is too small for the reaction to proceed, and all light which passes this depth is lost. The

minimum radiation temperature for spontaneity is found from eq 44

$$1 - T_0/T^*_{\min} = \Delta G_f/mN_0h\nu_0 \quad (67)$$

With the help of eq 42, 46, and 50 this may be written in terms of a minimum absorption rate

$$(k_0)_{\min} = \frac{k_1}{1 - \eta_2} \exp\left[\frac{\Delta G_f - mN_0h\nu_0}{mRT_0}\right] \quad (68)$$

The left-hand side may be written in terms of X_{\max} by making use of Beer's law and the relations of ref 75:

$$\int_0^\infty (N_0h\nu)^{-1} 10^3 \ln 10 \epsilon(\nu) \exp[-\ln 10 \epsilon(\nu) C_0 X_{\max}] I_0(\nu) d\nu = \frac{k_1}{1 - \eta_2} \exp\left[\frac{\Delta G_f - mN_0h\nu_0}{mRT_0}\right] \quad (69)$$

$I_0(\nu) d\nu$ is the incident radiation flux ($\text{erg cm}^{-2} \text{s}^{-1}$), $\epsilon(\nu)$ is the absorption coefficient and C_0 is the concentration. If the absorption is so strong that Beer's law fails, the nonlinear absorption coefficient of ref 72 may be employed. Once eq 69 has been solved for X_{\max} , the η_1 efficiency may be found from the number of photons absorbed to depth X_{\max} times $h\nu_0$, divided by the incident energy

$$\eta_1 = \frac{\nu_0 \int_0^\infty \frac{I_0(\nu)}{\nu} [1 - \exp[-\ln 10 \epsilon(\nu) C_0 X_{\max}]] d\nu}{\int_0^\infty I_0(\nu) d\nu} \quad (70)$$

Unlike eq 49, eq 70 is independent of arbitrary low-frequency cutoffs. Equations 69 and 70 are quite intractable for even the simplest $I_0(\nu)$ and $\epsilon(\nu)$, and above we have employed the η_1 efficiencies of ref 56. A future report will be dedicated to more reliable η_1 efficiencies.

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ADDITIONS AND CORRECTIONS

1984, Volume 88

Sidney Golden[†] and Thomas R. Tuttle, Jr.*: Limitation on Determining Excess-Electron Structures by Magnetic Resonance Methods.

Page 3781. In the first line of the abstract the phrase "position of the particle from its" should be replaced by the phrase "energy of a typical nuclear".