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10. Supported by NSF grant GB 32018X.

12 November 1974

We are pleased that Dagan *et al.* have found an earlier reference (1) than Reiss (2), whom we cited (3), on the production of alternating single impulses in a network of model neurons. The general properties of reciprocally inhibitory neuronal networks are discussed by Sherrington (4), who in turn cites a number of 19th-century examples of similar alternating behaviors, both experimental and theoretical.

We are also pleased that they have corroborated our statement [note 9 in (3)] that the precise mechanisms are not important for producing alternating burst patterns, but that the patterns “follow essentially from the phenomenon of burst production following cessation of synaptic inhibition.” The biphasic inhibitory-excitatory synap-

tic input of Dagan *et al.* is seen to be sufficient to produce a stable alternation of bursts. We have emphasized postinhibitory rebound (PIR) rather than such postulated components as high- and low-pass filters because PIR is a widespread phenomenon in many nervous systems and is a likely candidate for the mechanism underlying the production of such motor patterns.

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12 March 1975

power plant by using process B to split water, drawing heat Q from these reservoirs, and then reacting the hydrogen with oxygen in an ideal fuel cell, neglecting all irreversible losses. For each mole of H_2 produced we will get 57 kcal of electricity, using 30 kcal from source I, 26.5 kcal from source II, and 30 kcal from source III.

On the other hand, an ideal Carnot engine would generate only 37.4 kcal of electricity:

$$\Delta G = \sum Q_{\text{input}} (1 - T_{\text{ambient}}/T_{\text{input}}) =$$

$$30(1 - 300^\circ/373^\circ) +$$

$$26.5(1 - 300^\circ/623^\circ) +$$

$$30(1 - 300^\circ/873^\circ) = 37.4 \text{ kcal}$$

(where ΔG is the Gibbs free energy charge, and T_{ambient} and T_{input} are given in degrees Kelvin). Thus process B violates the second law of thermodynamics. What the authors neglect is the vast energies of separation [see (4)], which are even larger than appear from the above, as it is also necessary to generate the free energy lost in step B4. Otherwise, we could improve on the above perpetuum mobile by using step B4 to generate electricity in a fuel cell.

We have estimated the minimum separation work to be 37 kcal for process B and 45 kcal for process A. The separation processes generating this free energy are all carried out at low temperatures. In current practice, their real efficiencies ($\Delta G/Q$) are below 5 percent. The authors also underestimate the large irreversible heat loss incurred in heating the process streams to reaction temperature. The overall thermal efficiency for any of the three processes should be closer to 5 percent than to the 50 percent given.

Thermal efficiencies by themselves mean very little as no process can improve on the theoretical efficiency of electrolysis. It is the cost of obtaining it that counts. To put the cost in proper perspective, an ideal mass balance to produce 10^6 British thermal units (1 Btu = 0.95 kJ = 0.25 kcal) of hydrogen fuel or 16 pounds (1 pound = 454 g) of H_2 is given below (the units are those used in American industry).

To produce 10^6 Btu worth, or 16 pounds of H_2 , we would have to hydrolyze about 0.4 ton (1 ton = 908 kg) of $MgCl_2$ at high temperature with steam; manufacture 1 ton of concentrated hydrochloric acid (30 percent); dissolve 0.5 ton of copper in hydrochloric acid; disproportionate about 1.6 tons of CuCl in aqueous dispersion into $CuCl_2$ and Cu, with all the associated steps; crystallize 1.4 tons of $CuCl_2 \cdot 2H_2O$ in a multiple evaporator crystallizer; dry 1.4 tons of $CuCl_2 \cdot 2H_2O$ and drive off the water of crystallization; and melt, decompose, solidify, and cool 1.15 tons of $CuCl_2$ —not to mention all the filtering,

Thermochemical Hydrogen Generation: Heat Requirements and Costs

The costs and energy requirements of the processes for thermochemical hydrogen generation presented by Wentorf and Hanneman (1) are so grossly underestimated that it is highly questionable whether these thermochemical processes can compete with other hydrogen generation techniques. To demonstrate this I will discuss process B presented in (1), although the comments apply equally well to the other two processes discussed by Wentorf and Hanneman and to very similar cy-

cles proposed in (2) and (3). The chemical reactions and the thermodynamic data used in (1) are given in Table 1, together with the estimated heat requirements.

A simple thermodynamic argument shows that, if the heat requirements and thermal efficiencies were really as reported by Wentorf and Hanneman, we could build a perpetuum mobile of the second type. Assume that we have three heat sources, at temperatures $T_I = 100^\circ C$, $T_{II} = 350^\circ C$, and $T_{III} = 600^\circ C$. We could now build a

Table 1. Thermodynamic data and heat requirements from (1).

Step	Reaction	Reaction temperature (°C)	Energies (kcal) for reactions as written		Heat requirements*
			ΔH°	ΔG°	
B1	$2Cu(c) + 2HCl(aq) \rightarrow 2CuCl(c) + H_2(g)$	100°	-8	2	
B2	$4CuCl(c) \rightarrow 2CuCl_2(c) + 2Cu(c)$	30° to 100°	30	38	30 kcal at 100°C
B3	$2CuCl_2(c) \rightarrow 2CuCl(c) + Cl_2(g)$	500° to 600°	30	0	30 kcal at 600°C
B4	$Cl_2(g) + Mg(OH)_2(aq) \rightarrow MgCl_2(aq) + H_2O(l) + \frac{1}{2}O_2(g)$	80°	-38	-46	
B5	$MgCl_2(c) + 2H_2O(g) \rightarrow Mg(OH)_2(c) + 2HCl(g)$	350°	4	8	26.5 kcal at 350°C
Irreversible losses					15 kcal
Total heat input					101.5 kcal

*The heat required for the production of 1 mole of H_2

washing, scrubbing, and distillation steps, the magnitude of which is mind-boggling! All this is to be accomplished at an irreversible heat loss and energy requirement of only 200,000 Btu, or 15 percent of the stoichiometric heats of reaction, and a total heat requirement of about 2.1×10^6 Btu.

The capital and operating expenses for this enormous plant are said to be more than \$1 per 10^6 Btu of hydrogen, which is certainly a correct although misleading statement since Wentorf and Hanneman claim that the process can compete with electrolysis, which suggests that the total cost is expected to be somewhere between \$6 and \$10 per 10^6 Btu. How can one expect any such thing if comparison with the thermal efficiencies and costs of similar processes clearly lead to costs and heat requirements at least one order of magnitude larger?

The hydrolysis of $MgCl_2$ mentioned above is a commercial process, and the present heat requirements and cost of this step alone would account for the total mentioned by Wentorf and Hanneman. Let us examine the disproportionation of $CuCl$ into Cu and $CuCl_2$, which is the crucial step. The heat requirement, given by Wentorf and Hanneman, is 440,000 Btu. The equilibrium concentration of $CuCl_2$ in the presence of $CuCl$ in slightly acid aqueous solution is 0.3 g per liter. In two of the options mentioned we would need to treat 900,000 gallons (1 gallon = 3.8 liters) of water for each 10^6 Btu of H_2 generated. Wentorf and Hanneman state that the heat needed for the evaporation of water can be regained by condensation with "only a small loss." What does this mean? In the best equipment sold by the General Electric Company, the heat requirement for the evaporation of 900,000 gallons of water in a multiple-step evaporator would be 600×10^6 Btu. If there is a way to evaporate water with "small loss," let's forget about generating hydrogen and concentrate on watering the desert, since we are talking about the equivalent of desalinating 10^6 gallons of brackish water! Even if we were to find a very efficient chelating agent, the heat needed would still be 2×10^6 Btu in addition to the heat of reaction—and this in order to make 10^6 Btu worth of H_2 !

Even if we did not have to worry about the low equilibrium concentration, the mere crystallizing of 1.15 tons of $CuCl_2$ from a concentrated acid solution and drying it would require well above 10^6 Btu, and involve capital and operating costs well above \$5, making the whole process questionable just on the basis of this one idealized step alone.

And so on . . .

In the present state of the art, an optimistic cost estimate for process B would be close to \$100 for 10^6 Btu of hydrogen or more than \$600 for the fuel equivalent of one barrel of oil. This plant would be so big that it is doubtful that we could recover the energy invested in its construction. None of the other processes described in (1) seems much better.

We are not dealing here with some unknown future technology but with chemical and physical steps very similar to industrial processes that are at present widely used. If we are to find better processes for the generation of hydrogen as well as for any other new energy source, the research for them must be based on proper realistic estimates of heat and cost requirements.

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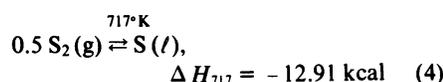
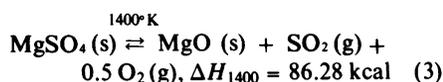
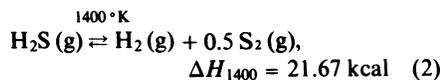
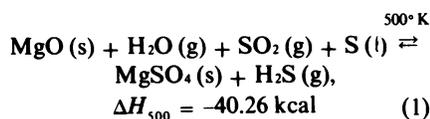
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30 August 1974; revised 30 December 1974

Wentorf and Hanneman have suggested (1) that, since the decomposition of many metal sulfates requires a large amount of heat (70 to 100 kcal/mole), closed thermochemical cycles based on sulfate chemistry will have low thermal efficiency. Our purpose here is to indicate that this conclusion is misleading. In fact, our group at the University of Kentucky has invented very efficient thermochemical cycles based on the decomposition of metal sulfates. Wentorf and Hanneman, in their definition for efficiency, assumed that all the heat released at low temperature is lost, and this is where their analysis is in error. The following example of a closed thermochemical cycle illustrates this:



(The S_2 in Eq. 4 is in reality a mixture of higher polyatomic molecules of sulfur; a combination of S_8 , S_6 , S_4 , and S_2 exists at 717°K.)

In this example the exothermic heat of reaction of Eqs. 1 and 4 is produced at over 500°K and therefore may be utilized for heating purposes or to produce work. Calculating the efficiency while assuming (i) a higher heating value for hydrogen, (ii) ideal work of separating the gaseous products, and (iii) that 30 percent of the exothermic heat available after heat exchange is converted into useful work, we obtain a thermodynamic efficiency, $\eta = 0.59$. This is a relatively high value when compared to other processes hitherto studied (2). The analysis utilizes the HYDRGN program developed at the University of Kentucky (2, 3).

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15 October 1974

The primary purposes of our article were to describe the underlying concepts for the selection of closed-cycle thermochemical processes and to use three cycles to illustrate the key principles and problems. As a result, we did not claim that cycles A, B, and C specifically chosen for this purpose were economically the most attractive or the most efficient or practical ones that exist even at present.

As we remarked in our article, closed-cycle thermochemical hydrogen will probably not be an economical source for at least two decades, if ever. Over the near term, open-cycle thermochemical processes based on coal and other hydrocarbons will certainly predominate, and, over the longer term, electrolysis and possibly other processes might displace the closed-cycle processes. Although a minimum conceivable cost for closed-cycle hydrogen of \$2.75 per 10^6 kilojoules (1974 dollars) was cited, the complexity and high capital costs of workable processes will escalate this figure considerably, according to our best estimates. For the above reasons and the very long time scale required for overcoming technical barriers, our closed-cycle thermochemical hydrogen ef-

fort has now been terminated in favor of open-cycle and electrolytic approaches.

Shinnar's comments illustrate the differences between the ideal and past or current practice, particularly in regard to recovering waste heat and minimizing the work required for separation. Considerable improvement would be needed in these areas in order to make closed-cycle thermochemical hydrogen economically feasible; one here must trade capital investment against operating costs to find the minimum total cost. We agree that a very important part of cycle selection, often ignored, is the minimizing of phase separation work by using "natural" phase separations as much as possible.

Processes A, B, and C do not violate the second law of thermodynamics, as implied by Shinnar. Specifically, if one supplies 18 kcal for losses and work at 600°C, and 30 kcal (for step B2) at 200°C, the ideal Carnot equivalent engine for process B would deliver 56.2 kcal, which is not far from the theoretical 56.7 kcal, considering possible inaccuracies in thermodynamic data and the simplified analysis. A proper analysis of processes A and C leads to the same conclusion.

The 1400°K thermochemical cycle proposed by Soliman *et al.* is quite similar to one that we evaluated earlier in our labora-

tory, and we agree that it looks relatively attractive on a heat efficiency basis. However, we hold to our earlier opinion that a limit of 1200°K seems realistic for safe process heat delivered across a heat exchanger in commercial reactors for the next two decades. For 1200°K maximum, the identified thermochemical cycles based on sulfates appear to involve unnecessary penalties in energy consumption. If the serious problems of heat exchanger integrity, corrosion, and containment of radioactive species at the 1400°K level can be solved, then the cycle of Soliman *et al.* or some other cycle could form the basis for a successful water-splitting process. Such a cycle might require integration in certain temperature ranges.

In summary, the basic concept of closed-cycle thermochemical hydrogen processes is sound but further detailed study will be required to determine whether they are practically and technically feasible and whether they will ever compete economically with electrolysis or other hydrogen production methods in the long term.

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20 March 1975

Iron and Susceptibility to Infectious Disease

One of man's most critical nutritional problems is iron-deficiency anemia (1). As Weinberg pointed out (2), however, administration of supplemental iron would be counterproductive if it did indeed neutralize an individual's defense against bacterial pathogens. Before we conclude, like the author of a recent letter to *Science* (3), that iron fortification of foods would be "irresponsible," we should take pains to determine whether the relevant experimental work in this area really supports Weinberg's arguments.

Serum transferrin is bacteriostatic because it binds available ionic iron and withholds it from bacteria, which require iron for growth. If transferrin iron-binding capacity is saturated, this potential bacteriostatic mechanism cannot operate. Many of the experiments designed to substantiate this function have been based on one of two assumptions: (i) that iron administered parenterally in the form of stabilized iron polymers, such as iron-dextran or ferric ammonium citrate, "saturate" circulating transferrin *in vivo*; or (ii) that iron-transferrin prepared *in vitro*, by adding inorganic ferric or ferrous salts, is identical

to iron-transferrin formed during the assimilation of iron *in vivo*. Neither assumption is valid.

Iron polymers react sluggishly, if at all, with transferrin (4, 5). Intravenous injections of polymers may easily deliver an amount of iron to the blood that greatly exceeds the iron-binding capacity of transferrin (6) before they are cleared from the circulation by the reticuloendothelial cells, which may then release a portion of this iron to transferrin for several days (7). After intramuscular or intraperitoneal injection of iron polymers, serum iron may equal or exceed the total iron-binding capacity for a few hours while the polymers are absorbed intact into the lymphatics (8). Such high concentrations of iron in the serum are only transient, but significant amounts of polymeric iron are meanwhile available for microbial growth. Under these circumstances, transferrin "saturation" have no physiological meaning. The data (6, 9) simply demonstrate that microorganisms can thrive on polymeric iron. The implications of these data should not be extrapolated to any but iatrogenic situations.

Stoichiometric Fe(III)-transferrin complexes are formed *in vitro* only when the ferric ion is presented to the protein in a suitably chelated form, for example, as iron nitrilotriacetate (10). Unfortunately, many widely used methods of saturating transferrin *in vitro*, including most current clinical procedures for measuring the total iron-binding capacity of human serum, continue to require inorganic ferrous or ferric salts as iron donors. Under such conditions, with O₂ present, ferrous ion is oxidized at a rapid rate at neutral pH, especially in the presence of serum transferrin or ceruloplasmin (11). The ferric ion formed by this oxidation immediately hydrolyzes to form polynuclear, high-molecular-weight complexes (12). When inorganic ferric salts are used to saturate transferrin, they rapidly hydrolyze to polymeric species and are in large part bound nonspecifically to the protein. All attempts to "saturate" transferrin with inorganic iron salts force the utilization of far more than stoichiometric amounts of iron to fill the two binding sites (5). The excess iron is present in a polynuclear form and is nutritionally available to microorganisms *in vitro* (13, 14).

As Weinberg noted (2), orally administered iron is generally not effective in promoting systemic infection. It is nearly impossible to saturate the transferrin of normal individuals by therapeutic oral doses of iron, partly because transferrin-bound iron is turned over rapidly in serum (15). Transferrin is not found fully saturated even after excessive intake of dietary iron in the rat (16) or man (17). There are no studies of bacteremia or systemic infections in animals whose serum iron levels were manipulated by strictly dietary means, that is, fed a low iron diet to produce iron deficiency or offered one of many suitable iron complexes which facilitate iron absorption and overloading (18). Experiments such as Kochan's (2, table 1; 14) are subject to the criticism that the variations in transferrin saturation were produced during the course of, or recovery from, an induced hypoferremic state, which may affect the levels of many other micronutrients or defense mechanisms. If there is real concern for the safety of dietary iron supplementation, it is important that experiments be developed with reasonable models to test the effect of transferrin saturation on bacterial infection *in vivo*.

The public health issues of dietary iron fortification are now being obfuscated by two arguments: The first is concerned with the potential danger of bacterial infection, as expressed in Weinberg's article; the second, with the danger that such iron will ex-

Thermochemical Hydrogen Generation: Heat Requirements and Costs

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Science **188** (4192), 1036-1038.
DOI: 10.1126/science.188.4192.1036

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