

# Up Front, Efficient Technology Evaluation: It's What's Needed to Prevent Futile Investments

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An important first step in the search for more effective or less expensive processes is to evaluate new ideas and research programs at a very early stage, preferably before any significant expenses have been incurred. This article presents a powerful and efficient method to do this using a minimal amount of data. It describes the approach and illustrates its use with an example from the public domain that is related to hydrogen (1–15). The H<sub>2</sub> economy has led to many research projects that make no sense, and vast government funds were and still are spent on them. For instance, the sums spent on thermochemically generated H<sub>2</sub> (\$10 billion spent worldwide in the 1970s, equivalent to \$30 billion in 2006 dollars) should raise severe concerns in our profession. If we want to continue to be leaders in technology and development in the present economic climate, it is important that we learn to be more cost efficient.

The method given here can be helpful in directing an organization to the more strategic use of its funds. It compares proposed processes with available technologies that are either similar or competitive, focusing only on the constraints of both—thermodynamic, kinetic and materials of construction, availability and properties of catalysts, separation routes, etc. It evaluates how the constraints affect the new process, or if the new process has different constraints, and then hones in on the differences between the processes and the economic value of any advantages or disadvantages.

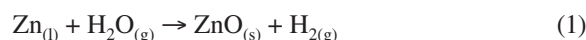
It is also helpful to try to understand why an existing process was developed the way it was. Before looking at any flowsheets or details, ask whether this idea makes sense and whether it is better than what is currently available. Prepare flowsheets and mass and heat balances, but do not rely on cost estimates based on these flowsheets, as the results are normally much lower than those found in practice. Flowsheets neglect many essential events of a real process. Ask how much the existing costs can be improved. Design involves many tradeoffs, and these tradeoffs will be different when the cost structure changes.

## Hydrogen production by thermochemical cycles

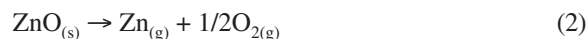
The high cost of hydrogen production using electrolysis led to the search for a less-expensive technology, one of which was thermochemical H<sub>2</sub>. A case in point is the standard process of H<sub>2</sub> generation from a nuclear reactor using the electricity to electrolyze water. This is expensive, so the idea was promoted in the 1970s to use the heat directly from a high-temperature nuclear reactor to split the water. However, the temperature required to split water directly is several thousand degrees Celsius, but the highest temperature at which heat can be transferred through a heat exchanger is 900°C. It was therefore proposed to use a closed set of chemical reactions along with the heat generated by the nuclear reactor.

The first thermodynamic principles demonstrate that it is not possible to find a cycle that can compete with a high-temperature nuclear reactor to generate electricity and electrolyze water (2). The program was therefore abandoned in the early 1980s, but has since been revived, and is receiving much attention.

**Cycle I.** To evaluate the efficiency of H<sub>2</sub> production using the zinc thermochemical process, consider the following:



where  $\Delta H = -25.4$  kcal/mol;  $\Delta G = -21.5$  kcal/mol; and  $T_R < 1,642$  °C.



where  $\Delta H = 114.4$  kcal/mol;  $\Delta G = 98.8$  kcal/mol; and  $T_R > 1,913$  °C.

Splitting water requires a large  $\Delta G$  input — 56.7 kcal/mol with  $\Delta H = 68.3$  kcal/mol. For a thermochemical cycle, this free energy increase must be generated by heat input (5). This means that  $\Delta H[(T_R - T_0)/T_R]$ , the free energy of the heat, must be larger than  $\Delta G$  for any endothermic reaction (6). In other words, the following must be true:

$$\Delta H > [T_R/(T_R - T_0)] \Delta G \quad (3)$$

Equation 3 can be used to compute the minimum reactor temperature needed to run the endothermic reaction with good conversion. If  $T_R$  is chosen to be 900°C, then  $\Delta H$  for any possible endothermic reaction is greater than 1.3 times  $\Delta G$ . For the dissociation of water, the ratio  $\Delta H:\Delta G$  is 1.06, and for ZnO, it is 1.16, which requires a temperature greater than 1,913°C. This cycle is not feasible using a high-temperature nuclear reactor. As previously mentioned, it is difficult to economically transfer heat through a heat exchanger at temperatures above 900°C, as required by the second reaction. If the condition in Eq. 1 is not fulfilled for the allowable temperatures, it does not mean that the process cannot be operated — it only means that the  $\Delta G$  cannot be generated by heat, and other ways to do so are needed. One of the most efficient and cheapest ways is by electrolysis, which is the current process. If the reaction involves a change in volume, compression or vacuum can be used to generate part of the  $\Delta G$ .

Another way to achieve the desired  $\Delta G$  is by separation processes. However, this is the least efficient route, as the efficiency of separation processes is normally between 5% and 20%. Before proceeding, consider a hypothetical question: Assuming a heat source can be found, such as solar power or a different high-temperature nuclear reactor, that allows us to

carry out the cycle — *Would this help?* Let's look at the thermodynamics. The theoretical thermal efficiency of the zinc cycle is the  $\Delta G$  of the splitting water (56.7 kcal/mol) divided by the  $\Delta H$  of the second reaction (114.4 kcal/mol), to give a quotient of 50%. The theoretical efficiency of generating hydrogen by first generating electricity, followed by electrolysis is 86%.

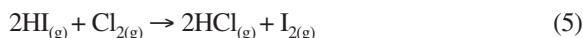
To compete with electrolysis on an equal basis (real efficiency is 40%), the practical efficiency of the thermochemical zinc route would have to be 80% of the theoretical, which no chemical process has ever achieved. In this route, we need to produce 33 kg of Zn from zinc oxide, and since 1 kg Zn cannot be produced for less than 30 cents, the cost of the zinc process would have been at least 10 times the cost of electrolysis (about \$1.00/kg Zn produced, including the cost of electricity) (13).

**Cycle II.** The idea was proposed to have a cycle with more reactions, such as the sulfur-iodine cycle shown in Tables 1 and 2 (7–9).

The first sulfur-iodine cycle proposed is a six-step cycle (Table 1). In practice it has several technical hurdles, including that the fourth and fifth steps are not feasible, as  $\Delta G > \Delta H$ . A similar problem exists for step 5. The reaction:



is the basis of commercial iodine production, but this step cannot be carried out as a single chemical reaction. In practice, chlorine made by electrolysis is added to the hydrogen iodide obtain iodine:



where  $\Delta H = -41.9$  kcal/mol and  $\Delta G = -41.8$  kcal/mol. The HCl is regenerated by electrolysis, resulting in a very expensive process. The only way to carry out step 5 directly is by creating the  $\Delta G$  by separation processes.

One way to conduct step 4 is to add water to the reaction. By doing so, the  $\Delta H$  and  $\Delta G$  become negative due to the strong negative  $\Delta H$  and  $\Delta G$  caused by the dissolution of  $\text{SO}_3$ . This is

Table 1. Sulfur-iodine thermochemical cycle I.

Step		$\Delta H$ , kcal/mol	$\Delta G$ , kcal/mol	T, °C*
1	$\text{SO}_{3(g)} \rightarrow \text{SO}_{2(g)} + 1/2 \text{O}_{2(g)}$	23.7	17.0	>780, (F)
2	$\text{SO}_{2(g)} + 1/2 \text{O}_{2(g)} \rightarrow [\text{SO}_{2(g)}] \text{ \& \ } [1/2 \text{O}_{2(g)}]$	n/a	0.7	(SP)
3	$\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$	10.5	2.1	(F)
4	$\text{SO}_{2(g)} + \text{I}_{2(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{SO}_{3(g)} + 2\text{HI}_{(g)}$	31.8	32.7	(U)
5	$2 \text{HI}_{(g)} \rightarrow \text{I}_{2(g)} + \text{H}_{2(g)}$	2.3	3.8	(RSP)
6	$\text{I}_{2(g)} + \text{H}_{2(g)} \rightarrow [\text{I}_{2(g)}] \text{ \& \ } [\text{H}_{2(g)}]$	n/a	0.4	(SP)
<b>Total</b>		<b>68.3</b>	<b>56.7</b>	<b>Water is split</b>

\*F = Feasible with heat from chemical reaction; U = Unfeasible as a chemical reaction, and impractical to combine with a separation process; SP = separation processes; RSP = Reaction feasible when separation processes provide the required free energy increase

Table 2. Sulfur-iodine thermochemical cycle II.

Step		$\Delta H$ , kcal/mol	$\Delta G$ , kcal/mol	T, °C*
1	$\text{SO}_{3(g)} \rightarrow \text{SO}_{2(g)} + 1/2 \text{O}_{2(g)}$	23.7	17.0	>780, (F)
2	$\text{SO}_{2(g)} + 1/2 \text{O}_{2(g)} \rightarrow [\text{SO}_{2(g)}] \text{ \& \ } [1/2 \text{O}_{2(g)}]$	n/a	0.7	(SP)
3	$\text{SO}_{2(g)} + \text{I}_{2(g)} + (n+2) \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)} + 2 \text{HI}_{(aq)}$	-36.2	-18.2	< 300, (F)
4	$2 \text{HI}_{(aq)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow [2 \text{HI}_{(g)}] \text{ \& \ } [\text{H}_2\text{SO}_{4(aq+)}]$	39.0	25.4	(SP)
5	$\text{H}_2\text{SO}_{4(aq+)} \rightarrow \text{H}_2\text{SO}_{4(l)} + n \text{H}_2\text{O}_{(g)}$	43.8	17.3	(SP)
6	$2 \text{HI}_{(g)} \rightarrow \text{I}_{2(g)} + \text{H}_{2(g)}$	2.3	3.8	(RSP)
7	$\text{I}_{2(g)} \rightarrow \text{I}_{2(c)}$	-14.9	-4.6	(F)
8	$\text{H}_2\text{SO}_{4(l)} \rightarrow \text{SO}_{3(g)} + \text{H}_2\text{O}_{(g)}$	42.1	21.6	>340, (F)
9	$(n+1) \text{H}_2\text{O}_{(g)} \rightarrow (n+1) \text{H}_2\text{O}_{(l)}$	-31.5	-6.3	(F)
<b>Total</b>		<b>68.3</b>	<b>56.7</b>	<b>Water is split</b>

\*F = Feasible with heat from chemical reaction; U = Unfeasible as a chemical reaction, and impractical to combine with a separation process; SP = separation processes; RSP = Reaction feasible when separation processes provide the required free energy increase.

an important principle in carrying out reactions with a high  $\Delta G$  — couple them with a strongly exothermic reaction that has a strongly negative  $\Delta G$ .

While this coupling is effective and allows the reaction to be carried out at a low temperature, it has a large penalty. Table 2 gives a detailed breakdown of all the steps. The overall reaction in step 3 has a strongly negative  $\Delta G$ , and as the sixth step is not feasible as a chemical reaction. Only 20.4 kcal/mol of the total  $\Delta G$  (56.7 kcal/mol) required are generated by chemical reactions, with a theoretical efficiency of 31% (practically less than 15%), a thermochemical cycle does not exist. And, since the free energy related to the reactions with a negative  $\Delta G$  is not useful (too low a temperature), only the positive  $\Delta G$ s must be summed up. The rest of the  $\Delta G$ , 36.3 kcal/mol, must be generated by separation processes.

But very few separation processes have efficiencies larger than 20%. Complex distillation has a  $\Delta G$  efficiency of 5–10%, and very few separation processes have efficiencies larger than 20%. Even without detailed cost estimates, we would need a nuclear reactor 3–4 times larger than required for electrolysis, plus very expensive chemical and separation processes. This would be hard to do for \$40/kg  $\text{H}_2$ , or \$300/million Btu  $\text{H}_2$ .

Considering the complexity of these cycles, a critical question arises: *Are there such cyclic processes in industry?* Yes, there still are, although there were many more in the past.  $\text{Cl}_2$  was originally made by a cyclic process, as were several other products all made now by electrolysis. When there is a need for a high  $\Delta G$ , electrolysis, when feasible, is far cheaper than a cyclic process. The situation is no different for  $\text{H}_2$ .

### Cost and efficiency considerations

As to the cost of electrolysis, consider a quotation from an actual manufacturer of the electrolysis systems; bearing in mind that the only plants available are small. Norsk Hydro Electrolysers AS (Oslo, Norway) (10) gave a quotation for a 1,000 kg/day  $\text{H}_2$  plant (atmospheric pressure) requiring 48 kWh/kg  $\text{H}_2$  and showing a higher heating value (HHV) efficiency of 82%, as \$1,450/kg  $\text{H}_2$  per day, including assembly. The investment cost of \$1,450 includes \$250 for off-sites also necessary for the thermal process. Although the net investment of \$1,200 could be significantly reduced by scale-up and mass production, we will continue to use \$1,200 for additional calculations in this article.

Here, we have to warn the reader of a common pitfall in technology evaluation. Researchers or managers trying to promote their ideas will maximize the cost of the competitive technology, while minimizing their own. For electrolysis plants, it is normal to see investment costs of several thousand dollars per kg  $\text{H}_2$  and an efficiency of 65% HHV for small units. While 65% was the efficiency 30 years ago, the cost of electrolyzers was never that high. We would advise the reader not to do so when evaluating his own ideas.

Note that the electrolysis is not a major cost in the production of  $\text{H}_2$ , compared to the cost of a nuclear reactor. An installed capacity of 2.2 kW is needed for each daily kg  $\text{H}_2$  (2 kW for electrolysis and 0.2 kW for compressors) (14). The cost for new nuclear reactors will vary widely; here, the cost is \$2,200 per kW used (15), which translates to \$4,840/kg  $\text{H}_2$  — much larger than \$1,200 for the electrolyzer.

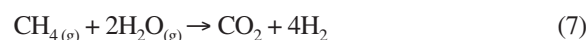
Thermal cycle plants will save the \$1,200/kg  $\text{H}_2$  for the electrolyzer and will also save \$800 for the part of the nuclear reactor that generates electricity. These numbers are based on the cost of a combined cycle power plant (\$400/kW capacity, commercial data). Actually however, only part of the \$800 is actually saved. The efficiency of a high-temperature nuclear reactor, 55%, multiplied by 0.82 yields 45%. Thus for 1 kg  $\text{H}_2$ , we need to supply to the process about 300,000 Btu (136,000/0.45). If the cycle could reach this efficiency, it would require the same heat input. This heat has to be delivered by circulating hot helium (185 moles or more for each kg  $\text{H}_2$ ) through the high temperature heat exchanger and nuclear reactor — four times more than is required in the electricity case, plus piping, and the cost of the high-temperature heat exchanger must be included as well. It might not be possible to do this for \$800 and definitely not for much less. But, let's assume \$400 can be saved for a total savings of \$1,600. This is about 20% of the total cost. Unless a cycle is more efficient than electrolysis, we can stop here.

The main question remaining is therefore: *Can a thermochemical cycle beat the efficiency of electrolysis?* The answer is an obvious *no*. The theoretical efficiency of electrolysis in HHV is 100%, and often the electricity generation is 80%. In chemical processing, even simple one-step reactions seldom reach 70% of theoretical efficiency in creating  $\Delta G$ , which is commonly 40%. For a four-step process, efficiencies will be a fraction of the theoretical efficiency.

This is illustrated by the simple example below involving  $\text{H}_2$  formation from natural gas. The overall reaction is:



where  $\Delta H = 10.5$  kcal/gmol and  $\Delta G = 2.05$  kcal/gmol



where  $\Delta H = 39.4$  kcal/gmol and  $\Delta G = 27.1$  kcal/gmol.

The efficiency of the high temperature reaction in creating a  $\Delta G$  is greater than 69%. The real efficiency of the process to increase the  $\Delta G$  by adding heat is 29% which includes steam generation and losses.

To make a valid comparison with electrolyzers, the theoretical value must be multiplied by a factor of 0.3 to 0.5 to get a real efficiency. In thermal chemical cycles, unlike electrolysis, the energy needs of the separation processes, and for moving the material around (including the hot helium) must be added to the total energy requirements. This energy requirement for pumping and moving material is, in most cases, substantial, especially when large quantities of material are involved.

While hundreds of cycles have been proposed, we have never seen a real one — a pure thermochemical cycle. So there are no examples of how high (or low) the efficiency of a thermochemical cycle is — only that it has to be below 25–30%. This example allows us to illustrate another useful method for process evaluation.

Assume the cost of electricity is \$0.06/kWh. Thus, the electricity will cost \$3.20/kg  $\text{H}_2$  (53 kWh, including compression). Assume the total cost of the electrolysis plant, \$0.60 including water purification and compression, is \$1,200/kg  $\text{H}_2$  per day. To estimate the cost of this investment per kg  $\text{H}_2$ , one has to compute the investment charges, such as depreciation, capital return, taxes, maintenance, operating costs, etc., to a cost per daily unit produced. This very strongly depends on how companies approach the required capital return. While these are complex computations, one can substitute for preliminary estimates a simplified formula: multiply the cost per daily unit produced by a factor of 0.0005 to 0.00075. For utilities the factor is closer to the lower limit. In practice the actual factor derives from the way the company computes it.

This gives \$32/million Btu (MMBtu)  $\text{H}_2$ , which, as a fuel, has a present value of \$8/MMBtu. Actually, the cost of the hydrogen is higher as we neglected in the comparison the cost of compression, storage, pipelining, etc., which would result in a minimum cost of \$45/MMBtu. We noted already

that the value of electricity, used directly as electricity, is at least double that of H<sub>2</sub>. So it is clear that whenever possible one should use electricity directly.

The high cost of obtaining hydrogen using electrolysis led to the idea of thermochemical H<sub>2</sub>. Regrettably, this process is not thermodynamically feasible, nor is it economically feasible. Let us look at the cost of a cycle for two cycles.

The first cycle requires 33 kg of zinc, which is derived electrolytically from zinc oxide. The cost of this reduction reaction is a major fraction of the cost of zinc, which is \$40 dollars/kg. There is no way to do this reduction for \$5/kg Zn or even \$10/kg Zn.

Now, let us look at the sulfur-iodine cycle (Table 2). Based on the overall production of 1 kg H<sub>2</sub>, 412 kg of material is processed in steps 1, 3, 6 and 8 and 253 kg of material is processed in the separation processes shown in steps 2, 4 and 5. The process also calls for 127 kg of I<sub>2</sub> per kg H<sub>2</sub> produced, and the concentration and decomposition of 100 kg of sulfuric acid. It is hard to see how this can be done for \$40/kg H<sub>2</sub> — not including the cost of expensive separation processes, which creates 66% of the  $\Delta G$ . Based upon industrial experience, it is safe to assume that creating 66% of the  $\Delta G$  by separation processes may be much more expensive and energy intensive than creating the whole  $\Delta G$  by electrolysis, and it will require a far bigger nuclear reactor. Thus, the money spent on a chemical cycle was in vain.

### Hybrid cycles

To overcome the difficulties of finding a real thermochemical cycle, a modified cycle based on the following reactions is presented:



where  $\Delta H = 34.1$  kcal/mol and  $\Delta G = 37.3$  kcal/mol.



where  $\Delta H = 23.7$  kcal/mol and  $\Delta G = 17.3$  kcal/mol.

The first step is carried out in an electrolytic cell, while the second step, a known process, takes place in a chemical reactor. As the cost and the losses of an electrolytic cell strongly depend on the amperage, the cost of the electrolytic cell is not likely to be less expensive than the electrolysis of water, since only 60% of the  $\Delta G$  is created in the cell.

Furthermore, the SO<sub>2</sub> formed at the electrode is likely to form H<sub>2</sub>SO<sub>4</sub>, doubling the free energy required for the second step, and thus destroying any further increase in  $\Delta G$  formed by the electrolysis. But the chemical reactions creating the remaining 40% of  $\Delta G$ , plus the free energy associated with the separation of SO<sub>2</sub> and O<sub>2</sub>, are less efficient and much more expensive processes than electricity generation. The cycle needs a larger nuclear reactor than required for the electrolysis, plus an expensive chemical plant. Without performing any experiments, one can already see that this cycle has no advantages. CEP

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