210b A Standardized Method for Evaluating the Potential of Alternative Thermochemical Cycles

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The most well-known thermochemical cycles are the sulfur cycles and the Ca-Br cycles. Their development is extensive, but not complete. Work is ongoing, especially for the sulfur-iodine thermochemical cycle and its variants. Over 200 other thermochemical cycles have been proposed in the literature, but these were not developed either because general interest in thermochemical cycles disappeared, because needed technology was not available, or because they were not suitable for a cyclic process. Interest in thermochemical cycles has now been revived as one means to produce the massive amounts of hydrogen required for facilitating the hydrogen economy or as a means to use off-peak power from nuclear plants. Using nuclear energy as a hydrogen source in place of fossil fuels reduces greenhouse gas emissions. Reexamination of the 200+ cycles in the literature and examination of cycles currently being proposed is therefore appropriate. The potential of these cycles should be determined prior to making a large investment in their development effort to identify and focus on the most promising ones.

The National Hydrogen Initiative (NHI) is supporting the development of a standardized methodology for evaluating thermochemical cycles for producing hydrogen. This method consists of the following three steps: (1) comparing proposed cycles against general or screening criteria, (2) calculating their idealized efficiency, and (3) assessing their chemical viability.

Screening criteria, the focus of the first step, would include general considerations such as the number and cost of the elements, the maximum temperature of the cycle, and the required voltage of any electrochemical steps. This allows some level of judgment of the merits of a cycle even if the overall chemistry and kinetics are poorly understood. For cycles using nuclear heat, the temperature of the heat source is limited to about 1200 K. Cycles that require higher temperatures should be eliminated for nuclear heat sources but may be suitable for advanced solar sources. Electrochemical reactions that require high voltages are energy intensive and will probably not be practical on that basis alone. Although the general screening criteria are simple to apply, they may be considered too broad in specific cases. For example, a cycle proponent may believe a cycle with an exotic metal holds sufficient promise that the impact of the higher capital costs might be negated. A new technology associated with the exotic metal might mitigate challenges associated with energy-intensive steps such as water handling, recycle, or separations such that O&M costs are drastically reduced. Therefore, the screening criteria should be used in an initial assessment, but with the understanding that exceptions might be appropriate when new technologies are available or when calculated idealized efficiencies are promising.

A calculation of the idealized efficiency, the second step, provides a quantitative measure of the minimum energy needed to produce hydrogen product. This is probably the most important criteria, since any cycle that is not economically viable will not be practical and will not meet DOE's cost targets NHI has developed a relatively simple method for calculating idealized efficiency that uses a simple spreadsheet approach. This calculation requires knowledge of the reactions' temperatures so that the appropriate heats of reaction, latent, and sensible heat can be calculated. In some cases, thermodynamic data is not available and must be estimated. Details of the estimation method should be provided. Work terms are also included. Electrochemical work is given by Faraday's law. Separation work is defined. Both are converted to their heat equivalent using a specified heat to electricity conversion factor, which is usually taken as 50%. Shaft work is ignored. The first calculation assumes idealized heat transfer. The second includes more realistic heat transfer using pinch analysis. Pinch analysis is a systematic method for optimizing energy usage.

The chemical viability of a cycle should also be addressed as the third step of the evaluation process. Some information on chemical viability can be obtained from the free energy of the various reactions. Generally, the free energy for each reaction should be ± 15 kcal/mol to avoid excessive energy loss in a cyclical process. However, some reactions with very favorable free energies do not proceed to completion because of slow kinetics or because of unexpected competing reactions. For elements that can exist in multiple oxidation states, separations may be difficult and should be considered explicitly. Necessary information on chemical viability may be obtained from the literature, from proof-of-principle experiments, or from the expertise of the cycle's proponent.

Screening Process for New Thermochemical Cycles

1. 1. Initial screening parameters and criteria for ranking if idealized efficiencies are comparable:
    1. a. The number of elements.
        1. i. Less is usually better than more; cycles with no more than 3 elements other than hydrogen and oxygen are recommended.
    2. b. The number of reactions.
        1. i. Less is usually better than more; cycles with no more than 3 or 4 reactions are recommended. For this initial screening, what constitutes a reaction may be defined as what can be accomplished in a single reaction vessel.
        2. ii. Two reactions can be combined into one if thermodynamic data are available for the reaction when combined but not when given separately.
    3. c. The likelihood of multiple products for a given reaction.
        1. i. Multiple oxidation states for a given element may result in a complex mixture of products that will be difficult to separate.
        2. ii. Oxy-hydrocarbon compounds, such as aldehydes and alcohols, usually show comparatively little selectivity in their reactions and are therefore not recommended. Data which suggests reactions with good selectivity may be considered.
    4. d. Relative costs.
        1. i. Noble metals, rare, or exotic materials may impact capital and operating costs negatively.
    5. e. Toxicity.
        1. i. Some metals have very low allowable EPA release rates (e.g., Hg, Se, and Cd) and may require special methods to limit their release or to immobilize waste streams.
    6. f. Maximum temperature requirement.
        1. i. Higher-temperature (>1075K) will require more exotic metallurgy, which will undoubtedly result in higher capital costs. Processes with lower maximum temperatures should be ranked above those with higher maximum temperatures.
    7. g. Corrosivity.
        1. i. Corrosion-resistant materials may not be available for a particular stream at desired operating conditions. A cycle that uses proven materials for reactors, etc., would have a higher ranking that one that requires new materials.
        2. ii. Corrosion products can contaminate product streams and catalysts
2. 2. Use NHI methodology to calculate idealized efficiency.
    1. a. Identify the thermodynamic database used.
    2. b. Identify unknown thermodynamic data and provide an estimation method for unknown data.
    3. c. Calculate an idealized efficiency.

      1. i. Determine reaction temperatures where free energies of reaction are acceptable.
      2. ii. Sum all heats of reaction plus sensible and latent heats to heat or cool a product stream from one reaction for the next reaction step.
      3. iii. Sum the work of separation for individual products from mixed gas or liquid streams.
      4. iv. Sum the potential work necessary to drive electrochemical reactions or those with positive free energy changes.
      5. v. Use Pinch Analysis or engineering judgment to make sure all heat recovery is done with positive temperature driving forces.
      6. vi. Identify the conversion factor for power and work into thermal equivalent.
   4. d. Eliminate those cycles whose idealized efficiency is less than some value, e.g., a conventional fossil power plant or other, about 35% (LHV).
3. 3. Use literature or proof-of-principle experiments to demonstrate chemical viability. Some questions to address (answers won't always be available):
   1. a. Do reactions go to completion as shown in the cycle?
   2. b. Are any undesirable by-products formed?
   3. c. What are the maximum concentrations of the reactants?
   4. d. Are there azeotropes or other non-ideal phases?
   5. e. How are by-products handled?
   6. f. How will separations be accomplished?
   7. g. Are new technologies required, e.g., such as high temperature, high pressure membranes?
   8. h. Are catalysts required? Will catalyst development be required?

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$$\varepsilon = -\frac{\Delta H_f\left(H_2O(g)(25°C)\right)}{\Sigma Q}$$