Present Status of Research in Hydrogen Production from Water by Thermochemical Cycles

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PRESENT STATUS OF RESEARCH IN HYDROGEN PRODUCTION

FROM WATER BY THERMOCHEMICAL CYCLES

by

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Summary

A brief discussion of the necessity of new fuel production methods for a future
hydrogen energy system is followed by an outline of currently available alternatives.
Of these only methods using fossil sources will be economically viable in the near
and midterm. Thermochemical methods, employing theoretically only water and heat will
only become competitive in the long range after depletion of fossil raw materials
has further advanced. A detailed discussion of currently favoured thermochemical
cycles closes the report.

Gegenwärtiger Stand der Kenntnisse auf dem Gebiet der thermochemischen Spaltung von Wasser zur Wasserstoffgewinnung

Zusammenfassung

Nach einer kurzen Diskussion über die Notwendigkeit neuer Brennstoffherstellungs-
verfahren für ein künftiges Energiesystem auf der Basis von Wasserstoff werden
die derzeit verfügbaren Alternativen skizziert. Wirtschaftlich entwicklungsfähig
in naher und mittelfristiger Zukunft werden aber nur diejenigen Verfahren sein,
die sich fossile Energiequellen zunutze machen. Thermochemische Verfahren, bei
denen theoretisch nur Wasser und Wärme eingesetzt wird, werden langfristig nur
konkurrenzfähig, wenn eine weitere Verknappung der fossilen Rohstoffe eintreten
sollte. Der Bericht schließt mit einer ausführlichen Diskussion der heute bevor-
zugten thermochemischen Zyklen.

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1. Introduction

Elemental hydrogen is a versatile element whose current importance is largely derived from its role as a major raw material in the chemical industry. For example, of the world production (1973) petroleum refining (hydrotreating, hydrodesulphurising, hydrocracking) consumed 42 %, ammonia synthesis for fertiliser production 37 %, chemicals (mainly cyclohexane) 9 %, methanol production 7 % and miscellaneous uses 5 %. Miscellaneous uses included, among others, uranium extraction and processing, foodstuff production and nylon and polyurethane manufacture. Despite this hydrogen is one of the least visible of all large volume chemicals. The reason being that over 93 % of all hydrogen produced is used captively: only 7 % is sold as merchant hydrogen.

1.1. Global consumption of hydrogen

In 1938 the worldwide consumption of hydrogen was $71x10^6$ m^3 whilst in 1973 the estimated annual total amounted to over $250x10^9$ m^3. Consumption of hydrogen in the US,for example,has grown by a factor of 40 since 1945 and has tripled in the last decade. Furthermore the demand for hydrogen is increasing: a recent NASA study[1] predicts two future possibilities (a) a reference scenario assuming continued historic uses with some new uses (mainly coal gasification and liquefaction) and (b) an expanded scenario including new future uses for example, as a gaseous fuel in home and industry, in steelmaking and as a liquid fuel for aircraft and ground transport.

Scenario a) projects increases in usage by factors of 1.7 and 5.5 by the years 1985 and 2000 respectively while scenario b) envisages increases of 3.4 and 20 for these time periods.

1.2. Hydrogen production: situation and alternatives

Presently about 90 % of the hydrogen manufactured arises via primary fossil fuels in processes whose general chemistry can be represented by the equations 1,2

$$CH_4 + H_2O \rightarrow CO + 3 H_2 \qquad\qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 . \qquad\qquad (2)$$
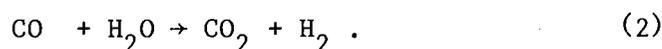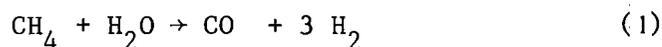
Petroleum refining operations e.g. catalytic cracking and reforming supply 45 %, another 45 % are derived from reforming of natural gas and the remainder arises from other sources such as coke manufacture, water electrolysis and fuel oil refining.

The dominant processes are however economical largely because of the currently low and often regulated (U.S.A.) price of natural gas and petroleum. For instance with a natural gas price of $ $0.75/10^6$ BTU hydrogen produced from it costs approx. $ $1.50/10^6$ BTU. Hydrogen produced from crude oil at $ 9.00/barrel or from coal will cost approximately $ $3.25/10^6$ BTU and $ $5-6/10^6$ BTU respectively.

Until the price of natural gas escalates significantly, because of increased costs of production, deregulation or other factors none of the alternative methods for hydrogen production appears to have an economic advantage. However because of the limited supply natural gas is not a suitable long term source for hydrogen. If the natural gas price rose to $ $1.00/10^6$ BTU hydrogen would rise in price to $ $2.50/10^6$ BTU (the heat content of 10^3 SCF of natural gas is about 10^6 BTU).

An attractive future role[1] for hydrogen would be its employment as a secondary energy carrier, either for storage or transmission, that is conversion to a "hydrogen economy" in which hydrogen would replace some or all other fuels.

Hydrogen presents almost unique advantages as an energy source:

1) it is by far the most environmentally sound energy carrier.
    (Apart from water only nitrogen oxides and some hydrogen peroxide
    are formed on combustion).

2) direct usage or conversion to other forms of chemical energy
    (ammonia, methane, methanol) is simple and the necessary technology
    available.

3) direct conversion to electricity by means of fuel cells is possible.

4) storage methods for gas, liquid or solid forms are available.

5) transportation in pipelines either as liquid or gas practically
    without loss, is possible and is already commonly performed over

distances >200 km within large chemical complexes.

Expansion of hydrogen into the world energy economy will however not be possible employing current production methods and will require new sources and improved production efficiency. Current sources being based on rapidly diminishing fossil materials it is apparent that future large scale production of hydrogen as an energy carrier can be only be founded on the only renewable source of hydrogen available; water. The decomposition of water into its elements can only be affected by considerable expenditure of energy. At present four major methods are available:

   i) electrolysis – a well established, reliable and simple process. The efficiency of conversion of electricity to hydrogen and oxygen is ≥ 80 %. The disadvantage lies in the efficiency of conversion of heat to electricity (<40 %). The high cost ($\$$ 10-15/10^6 BTU) of electrolytic hydrogen produced by conventional equipment is reflected in its low market share (1 %). Technological goals set for 1990 envisage development of advanced electrolysers providing electrolytic hydrogen at $\$$ 7-12/10^6 BTU for electric power costs of $\$$ 0.015-0.30/KWh^2.

  ii) direct thermal cracking is possible at elevated temperatures (>2000°C) because the free energy of water decreases markedly as a function of temperature. At 2700°C water is dissociated to ca. 1 % and contains around 0.65 % hydrogen. The technique is however not a practical alternative mainly because of material and recombination problems at such temperatures. Research on this topic has however recently been reactivated by the advent of high temperature solar furnaces[3].

iii) chemical reactions – although many reactions are capable of producing hydrogen, carbon is the only element available which is both sufficiently abundant (as coal) and is also a primary source of energy. Although the reaction

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

is well known, the disadvantages arising from the polluting nature and global distribution pattern of coal are evident. Another alternative, the steam-iron process (reactions 3,4) although employed late into the 1930's for supplying small quantities (<10^6 SCFD) of very pure hydrogen is no longer currently favoured.

$$Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \quad (3) \quad \text{oxidation}$$

$$Fe_3O_4 + CO \rightleftharpoons 3Fe + CO_2 \quad (4) \quad \text{reduction.}$$

The discovery of steam reforming in the 1930's made possible the production of much larger volumes of high-pressure hydrogen at lower cost[4a].

iv) thermochemical cycles - these consist of a series of chemical reactions conducted at different temperatures in which essentially thermal energy is transformed into chemical energy. Their attractiveness is based on the theoretical possibility of achieving higher thermal efficiences for converting heat into hydrogen than converting heat into electricity and electrolysing water. Definitions of the various efficiencies involved are shown in Figure I[5].

Figure I: definition of efficiency coefficients in the electrolytic and thermochemical production of hydrogen from water.

$$n_{thel} = E_{elec}/Q_{elec} \quad (5) \quad \text{(thermoelectric efficiency)}$$

$$n_{elec} = E_{rev}/E_{eff} \quad (6) \quad \text{(electrical efficiency)}$$

$$n_{thermochem} = \Delta H/Q \quad (7) \quad \text{(thermal efficiency)}$$

$$n_{ech} = \Delta H/E_{elec} \quad (8) \quad \text{(electrochemical efficiency)}$$

where E_{elec} = electrical energy for water splitting

Q_{elec} = thermal energy required for electrolysis

E_{rev} = reversible cell potential (theoretical)

E_{eff} = effective cell potential

ΔH = enthalpy of water splitting

Q = necessary heat energy

In general, electrochemical efficiences for conventional cells lie around 85 %, the electrical efficiency around 65 % and the thermal efficiency 20-30 %. Thermal efficiencies estimated for various thermochemical cycles vary from a pessimistic 18 % to 47-60 %[5a].

A generalised scheme for a thermochemical cycle is shown below[6]:

$$2AB + 2H_2O = 2AH + 2BOH \qquad (\Delta G \cong 0, \Delta H < \text{at } T_1) \qquad (9)$$

$$2BOH \qquad = 2B + H_2O + N_2O_2 \quad (\Delta G \cong 0, \Delta H > 0 \text{ at } T_2) \quad (10)$$

$$2AH \qquad = 2A + H_2 \qquad\qquad (\Delta G \cong 0, \Delta H > 0 \text{ at } T_3) \quad (11)$$

$$2A + 2B \qquad = 2AB \qquad\qquad (\Delta G \sim 0, \Delta H < \text{at } T_4) \qquad (12) .$$

Net reaction $H_2O \rightarrow H_2 + 1/2O_2$

where T_2 and T_3 are substantially higher than T_1 and T_4. The remainder of this report will be confined to a discussion of such cycles, their current status and possible future developments.

2. Thermodynamics of closed thermochemical cycles

The thermodynamic derivation of the efficiency of converting heat to hydrogen is presented elsewhere[7], hence only the main conclusions are summarised here as follows:

1) for maximum efficiency each reaction of a thermochemical cycle should be carried out at a temperature at which its standard Gibbs free energy ΔG^o vanishes,

2) the sum of the enthalpies of reaction must equal or exceed the enthalpy of formation of water.

3) if external work ($\Delta G \rightarrow 0$) is to be minimised we deduce from (13)

$$\Delta G = \Delta H - T \Delta S \qquad\qquad (13)$$

that this can be achieved practically by operating reactions with positive entropy changes at high temperatures and those with negative changes ΔS at low temperatures.

2.1.   Practical requirements for a thermochemical cycle

Hundreds of water decomposition processes have been proposed. Of those published, many are purely conceptual with no substantiating experimental verification and none have been demonstrated in a closed loop mode on a prototype or pilot plant basis. Very few of the proposed cycles would be even potentially useful as hydrogen sources for industrial uses. Some of the more frequent deficiencies are as follows:

i)   primary reactions do not take place rapidly enough or complicating side reactions occur.

ii) many of the more attractive cycles require that major portions of the total process heat be delivered at too high temperatures, frequently to solids.

iii) frequently rare, expensive or environmentally unacceptable chemicals in large tonnages are employed, thus placing severe restrictions on the basic chemistry, usuable construction materials and increasing the potential investment costs. The ideal thermochemical cycle for water decomposition should accomplish two goals i) minimise product cost by high thermal efficiency in a process with low capital and operating costs and ii) maintain the efficiency over a range of heat source temperatures, thereby allowing flexibility the choice of heat sources and construction materials.

Unfortunately only a few cyclic processes have been devised which combine more than one or two of the above requirements. Virtually all require some ΔG input in the form of pumping work in order to seperate components and overcome chemical irreversibilities. This may, in the worst cases reduce efficiencies to lower than that of conventional electrolysis (see 1.2). Two step thermal processes might be more efficient but none are known with $\Delta G = 0$ for both steps. Therefore processes involving a high temperature step with $\Delta G \doteq 0$ combined with a low temperature step of negative ΔG which may be provided by electrolysis may be of interest for practical hydrogen production.

2.2. Some proposed thermochemical water decompositions processes

Research on the production of hydrogen by the thermochemical decomposition of water began around 1970. Until recently attention had been generally focussed on the definition of a large number of cycles possessing the necessary thermodynamic properties. For this purpose computer programs capable of selecting cycles on the basis of their predicted thermal efficiency were widely prepared. Bamberger[8] has recently provided a compilation of 129 published cycles available to mid-1978. A selection of these is presented in Table I. Of those listed 4-5 have emerged as candidates for further laboratory or pilot plant investigations. The remainder of the cycles proposed in Table I, though demonstrating favorable thermodynamics have not progressed beyond the testing of some of the reactions involved and thus will not be further discussed here. The rest of this report will be concerned with discussion of their status as of December 1978.

3. Current Status of favored thermochemical water splitting cycles

3.1. The General Atomic Sulphur dioxide - Iodine Cycle[9a]

This cycle has been known for a number of years and has been studied in several alternative forms[9b]. At its simplest it can be described by the equations in Table I: Cycle 3. The cycle has a number of favourable properties. Depending on the temperature at which the first reaction is carried out the cycle can involve only fluids. The products of the key reaction (HI and H_2SO_4) can be easily pyrolysed in reactions which may be accelerated catalytically, thus generating hydrogen and iodine/SO_2 for recycling.

3.1.1. Main areas of R and D activity

3.1.2. Basic chemistry of SO_2-I_2-H_2O system

An aggravating problem in this cycle has been that of separating the HI and H_2SO_4 cleanly from one another. If the reactants are used in a

stoichimetric ratio yields are very poor.

$$SO_2 + I_2 + H_2O \rightleftharpoons H_2SO_4 + 2HI \qquad (14)$$

To improve this it is necessary to run the reaction using an excess of
one of the input components. Two approaches have been made to alleviate
this problem i) use of an excess of iodine, thus creating two liquid
phases. One containing a concentrated aqueous solution of sulphuric acid
and the other (HI_x) containing the unreacted iodine, HI and unreacted
water. Cross contamination of acids is reported to be minimal[9a], and ii)
working with an excess of SO_2 in liquid SO_2. Here HI is preferentially
dissolved in the SO_2 rich phase. The seperation is however only acceptable
when the reaction is not run to completion; if complete reaction of I_2 is
allowed must of the HI was found finally in the aqueous phase, together
with the sulfuric acid. With the exception of iodine all chemicals involved
in this cycle are fluid. Hence efforts have been made to run the reaction
at temperatures above the melting point of iodine[9a]. First results suggest
higher efficiency and easier operation. The best yields above the melting
point approach the yields at 95° although they require nearly 30 % more
iodine.
The key reaction (14) appears to be unaffected by oxygen in the reagent
mixture. Thus it may be possible to run it with the offgases from the
sulphuric acid decomposition without further purification.

3.1.3.   The hydrogen generating step: catalysis and separation problems
         in the decomposition of hydrogen iodide

The limited studies of the heterogeneous catalytic decomposition show that
substantial rate increases can result from the use of catalysts. The lower
temperatures obtainable have several advantages 1) material problems will
be less severe 2) it may be possible to use conditions under which liquid
state iodine is produced, thus increasing the potential conversion per pass.
A catalyst is required which provides a sufficient rate at low temperatures
and in the presence of condensed iodine. Presently only activated charcoal
has been confirmed as a catalyst in the temperature region from 375-550°K.
The activity drops by a factor of 100 however in the presence of liquid
iodine.
Another method of decomposition of HI and separation of hydrogen in one

step is based on the high pressure - low temperature reaction[11]. At a
pressure of 60 bar and 200°C a 21 % conversion to liquid iodine was
achieved, competitive with the gas phase equilibrium conversion at 600°C.
The core of the apparatus is a palladium - silver membrane in which
hydrogen is simultaneously seperated.

3.1.4. The catalytic decomposition of sulphuric acid[9a-c]

The rate of the homogeneous catalysed reaction is basically too slow
at accessible temperatures to be feasible commercially. The catalytic
properties of the oxides of the first row transition elements have
recently been compared. Generally although catalytic activity is apparent
their utilisation is questionable because of vapor transport (Cr_2O_3, V_2O_5)
or sulfation (Cu,Mn,Fe) in the $H_2O-SO_2-SO_3-O_2$ atmosphere. Though there
seem to be possibilities for the better transition metal catalysts the
platinum based catalysts investigated by Norman et al.[9b] are effective
at lower temperatures.

Westinghouse investigators[24] have conducted 1000 hr lifetime tests on
V_2O_5 and Pt catalysts chosen for the SO_3 reduction step. The vanadium
catalyst showed a reduction in activity of 7 % at 850° while platinum,
although showing lower initial activity, maintained its activity over
the test period.

Actually the regeneration of sulphuric acid from spent acid via thermal
decomposition already replaces 9 % of the conventional raw materials for
sulphuric acid production. With the enforcement of severer pollution
restrictions this might finally increase to more than 50 %[33].

3.1.5. Material corrosion investigations

Assessment of potential construction materials for corrosion resistance
to anticipated process fluids has been carried out by the General Atomic[12]
and Ispra[13] research groups.

In 1000 hr tests bare alloys, Incoloy 800H, Inconel 600 and stainless steel
showed selective internal corrosion along grain boundaries during treatment

with decomposing sulphuric acid vapour at 1173 K. Surface coated aluminised
Incoloy 800 H however showed excellent resistance to the severe oxidising
environment and was selected as candidate material for heat exchangers.
Titanium, zirconium, tantalum, niobium and molybdenum showed excellent
corrosion resistance to hydrogen iodide at $295^{o}K$.

Some flourocarbon plastics, a perflourocarbon elastomer, borosilicate glass
and a few carbon materials exhibited resistance to attack in HI_x. In Ispra[13]
recent efforts have been concentrated on tests involving sulphuric
acid corrosion resistance. Again the conclusion is that the bare commercial
materials are unlikely to have adequate corrosion resistance. Certain ceramic
materials are compatible but their use will be limited in a real plant.

3.1.6. Use of the cycle in solar generation of hydrogen[14]

A basic problem in coupling a solar heat source to water splitting arises
because of the diurnal nature of the radiation and fitting this to permit
a uniform level of hydrogen production over a whole day. The GA Sulfur-
Iodine cycle may lend itself to this purpose since the intermediate compounds
are storable. The collector mirrors are divided into high and intermediate
temperature regions. The low temperature solution reaction is conducted
24 hrs/day, producing H_2SO_4 and HI. The H_2SO_4 is stored and during daylight
is decomposed in the high temperature region. The intermediate temperature
mirror field heats a heat transport fluid (eutectic salt) providing heat for
concentration and cracking the HI. At night these functions continue but the
mirrors are bypassed on the way to a heat storage reservoir.

General Atomic is developing simple low cost fixed mirror solar collectors
(FMSC) with concentration factors of 206 suns compatible with the process[15].

3.2. The Ispra Mark 13 Cycle[16]

The relevant equations are shown in Table 1: Cycle 4. Use of the element
bromine leads to sub-cycles in which hydrogen bromide must be decomposed.
The relatively high heat of formation of HBr has a dual effect a) the
energy consumption for its decomposition is high and b) H_2SO_4 and HBr can
be obtained at high concentration and in different phases.

3.2.1. Main areas of R and D activity

3.2.2. Basic chemistry of the SO_2-Br_2-H_2O system

Although the reaction yielding HBr and H_2SO_4 is quite well known, equilibrium
data are still rather sparse. From the results of experiments conducted at
Ispra it could be demonstated that provided an excess of bromine is present
the equilibrium lies well to the right and practically no SO_2 remains in
the gas phase if the relative sulphuric acid concentration in the liquid
phase is below 0.65. High conversions of SO_2 (91 %) were also observed in
dynamic experiments involving countercurrent dual column reactors[17].

3.2.3. The hydrogen generating step: electrolysis versus chemical subcycles
        in the decomposition of hydrogen bromide

Basically two methods are available for the decomposition of HBr in the
hydrogen producing step i) electrolysis, ii) thermal decomposition with
or without a chemical subcycle.

Comprehensive work at Ispra[18a-c] on the electrolysis of HBr has demonstrated
its feasibility on a laboratory scale with bipolar graphite electrodes.
The high hydrogen overvoltage on graphite can be reduced by adding small
amounts of palladium or platinum directly to the electrolyte. Current
densities of more than 8000 A/m^2 at 1 V were observed at a cell temperature
of 373°K using 50 % HBr. The feasibility of the step on a technical scale
however remains to be demonstrated. Workers at Saclay have achieved current
densities of 9000 A/m^2 at a voltage of 0.9 V and 150°C using smooth platinum
electrodes in 47.5 % HBr.

Recent work in Los Alamos has been concerned with the decomposition of HBr in
a chemical subcycle. The base hydrolysis (reactions 15-18) of ferrous bromide

$$3FeBr_2 \text{ (aq)} + 3MgO(s) \rightarrow 3FeO(s) + 3MgBr_2 \text{ (aq)} \qquad (15)$$

$$3FeO \text{ (i)} + H_2O \text{ (g)} \rightarrow Fe_3O_4 \text{ (s)} + H_2 \text{ (g)} \qquad (16)$$

$$3MgBr_2 \text{ (aq)} \rightarrow 3MgBr_2 \text{ (s)} \qquad (17)$$

$$3MgBr_2 \text{ (s)} + 3H_2O \rightarrow 3MgO + 3Br_2 \text{ (g)} \qquad (18)$$

was found to be a method for splitting HBr thermochemically.

All the reactions occur at relatively low temperatures so that coupling to solar heat sources might be possible. The formation and subsequent dehydration of magnesium bromide incurs however an extremely large heat penalty since it will be impossible to match it with the low temperature exothermic wasteheat.

Lessart et al.[19] have investigated two step thermochemical subcycles for the decomposition of HBr

$$2 \ X + 2HBr \rightarrow 2 \ X \ Br + H_2 \qquad (19)$$

$$2 \ X \ Br \qquad \rightarrow 2 \ X + Br_2 \qquad (20)$$

where X is a metal bromide, oxybromide or oxide. Nine metals were considered; Cr, Cu, Fe, Mo, Pb, Sn, Ti, V and W. Of these the most promising appears to be a cycle involving vanadium.

$$VBr_2 + HBr \rightarrow VBr_3 + 0.5H_2 \qquad (21)$$

$$VBr_3 \qquad \rightarrow VBr_2 + 1/2 \ Br_2 \qquad (22)$$

It appears possible to conduct the VBr_2 - HBr reaction at low temperature and high pressure even in the presence of moisture without the risk of side reactions. The decomposition of HBr by this method will consume approx. 45 Kcal/mole of hydrogen obtained. According to these authors the thermal efficiency of Mark 13 modified in this way would be approximately 48 %.

3.3. The Westinghouse hybrid sulphur cycle

The chemical basis for this simple two step thermoelectrochemical cycle is shown in Table 1: Cycle 2. The net result of the reactions is the decomposition of water into hydrogen and oxygen. Sulphur oxides are involved as the recycling intermediates. Although electrical power is required in the electrolyser much smaller quantities(approximately 15 %) are needed than in conventional electrolysis (theoretical 1.23 V, practical ca. 2 V). Thus the ratio of heat to work required to decompose water are expected to be increased, leading to an increase in thermal efficiency.

3.3.1. Main areas of R and D activity

3.3.2. The electrochemistry of the SO_2-H_2O system

Despite its apparent simplicity the basic electrochemistry[22] of the system continues to be of interest. Appleby and Pichon[23] have recently reported a study of SO_2 oxidation in sulphuric acid solution as a function of acid concentration using platinum electrodes of high surface area. The process is highly irreversible apparently proceeding via a dithionate intermediate:

$$H_2O + SO_2 \rightarrow (H_2SO_3^+) \text{ ads.} + e^- \qquad (23) \text{ (rapid)}$$

$$2H_2SO_3^+ \rightarrow H_2S_2O_6 + 2H^+ \qquad (24) \text{ (rate determining)}$$

$$H_2S_2O_6 \rightarrow H_2SO_4 + SO_2 \qquad (25)$$

$$2SO_2 + 2H_2O \rightarrow H_2S_2O_6 + 2H^+ + 2e^- \qquad (26)$$

Applying the Nernst equation to the electrochemical half reactions 23 and 24 and rewriting in net reaction form we get;

$$E = E_o + \frac{RT}{2F} \ln \frac{a_{H_2S_2O_6}}{(P_{SO_2}) \cdot (\alpha_{H_2O})^2} \qquad (27)$$

values of $\sim$ E of 0.52 V and 0.7 V for acid concentrations of 65 % and 85 % respectively at $60^{o}C$. These, then represent the minimum ΔG values for the conversion if the dithionate mechanism is correct. Although the reaction is not catalytic in the normal electrochemical sense it is strongly substrate dependant, probably involving only physisorption. The results of this study suggest that a simple flow type cell[*) using 50 % sulphuric acid will probably be optimal in a practical process.

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*)
The successful operation of such an electrolyser requires that SO_2/H_2SO_3 be excluded from the cell catholyte otherwise the reaction

$$H_2SO_3 + 4H^+ + 4e^- \rightarrow S + 3H_2O \qquad (28)$$

occurs, depositing sulphur thereby reducing recyclability and adversely influencing cell performance. Other than flow cells various ~~othter~~ methods based on diaphragms are available[23].

The overall efficiency will however be influenced by the higher than calculated cell voltage. The feasibility of the process will therefore be intimately connected with its practical efficiency and necessary capital costs. Westinghouse investigators consider the feasibility as already proven[24]. Cell voltages of 600 mV are currently achievable, while 410 mV is projected at the time of writing[24].

3.4. The Zinc-Selenium cycle of the Lawrence Laboratory[26a-c]

The reactions constituting this cycle are shown in Table 1: Cycle 6. The cycle shown there is the newest in a series of several amended versions, the alterations having arisen largely because of problems encountered in development (e.g. slow hydrolysis reactions, poor thermal compability of some reactions). This cycle has not yet advanced beyond the stage of laboratory scale investigations of the individual reactions in olved to determine their potential applicability. Some flow sheeting, process design and preliminary cost estimates have been made.

3.4.1. Main areas of R and D activity

3.4.2. Basic chemistry of the cycle

The reaction between zinc oxide, selenium and sulphur dioxide, in which selenium is bound longer than in any other step, is considered the most critical in the cycle. Optimum operating conditions have not yet been defined though conversions of over 99.5 % have been achieved with high reaction rate at $723^{\circ}K$. Molten salt catalysis may be necessary to lower the reaction temperature while maintaining sufficiently high rates.

The reaction between dilute or concentration aqueous HCl and ZnSe proceeds rapidly ($\sim$ 95 % yield in 5 min). Most of the $ZnSO_4$ (from the $ZnO/Se/SO_2$ reaction) must however be seperated prior to hydrolysis to minimise the amount of HCl required. The thermal decomposition of zinc sulphate has been extensively investigated[26a-c]. The reaction is strongly endothermic and requires the highest temperature input for the cycle. Heat and mass transfer effects limit the reaction rate unless precautions are taken.

The hydrogen production step, the H_2Se decomposition reaction, should proceed spontaneously at room temperature, kinetics are however very slow. Decomposition is 60 % complete at 748°K in about 5 min. The maximum yield is expected to be around 65 % so that recycling will be required to completely decompose the H_2Se.

Taking the overall thermal efficiency of the process and using a conceptual battery design, Krikorian estimates a hydrogen production cost of $ 13.4/GJ (including nuclear heat). The cost of the HTR reactor (∿ M$ 520) was a modified value taken from the conceptual study by Westinghouse[21]. The cost of the chemical plant is estimated at M$ 855. In general, cost figures for other thermochemical cycles ranging from $ 4.65-11.65/GJ have been reported[27].

The inventory of selenium (500 tons) required for a plant of this size (27.3 tons H_2/hr = 2.25 Gm^3/yr at 80 % plant capacity) will obviously cause problems. The authors observe however that recovery of the selenium released from the smoke stacks of coal burning plants and coppersmelters would be amply sufficient for selenium based thermochemical plants.

3.5.   The mercury-Iodine Cycle (ANL-4) of Argonne National Laboratory[28]

This cycle differs from the other halogen employing cycles discussed above in that the hydrogen generating step does not involve the free hydrogen halide rather the easily volatile ammonium iodide is pyrolysed in a reaction involving mercury vapour.

3.5.1.   Main areas of R and D activity

3.5.2.   Basic chemistry of the cycle

This cycle consists of the following reactions.

$$2H_2O + 2NH_3 + 2CO_2 + 2KI_{(aq.)} = 2KHCO_3 + 2NH_4I_{(aq.)} \quad (29)$$

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2 \quad (30)$$

$$Hg + 2NH_4I = H_2 + 2NH_3 + HgI_{2(g)} \quad (31)$$

$$K_2CO_3 + HgI_2 = 1/2\ O_2 + CO_2 + Hg + 2KI_{(liq.)} \quad (32)$$

Strong points in its favour are the facts that i) the highest temperature at which heat must be delivered is ∿1000°K (Reaction 32), ii) reactions 2 and 3 can be driven at 475° and 600°K respectively, thus allowing facilitated coupling of the process to the stream of coolant from an HTR, and iii) all high temperature reactions proceed to virtual completion with acceptable kinetics and no solid materials need to be transferred at elevated temperatures. The presence of elemental mercury and the necessity for processing large volumes of solvent (see below) will render the technical realisation extremely questionable. For the most part current investigations are largely concerned with demonstrating the reliability of the individual reaction steps.

Water fed into the cycle in reaction 29 is spontaneously separated into its elements by ionisation, hydrogen becoming attached to ammonia and oxygen to the HCO_3^- ion. The most practical separation consists of first precipitating $KHCO_3$ and subsequently isolating NH_4I by evaporation of solvent. Direct evaporation is however severely penalised in terms of the expected thermal efficiency. At an expected concentration of 10 mol%, 20 moles of solvent would have to be vapourised for every 2 moles of NH_4I recovered (every mole of hydrogen produced).

Currently the most promising alternative involves vapour compression distillation of a solvent consisting of a 50 mol% aqueous solution of isopropanol. The work involved need only be ∿30 % more than the thermodynamic energy required to separate the solute reversibly and hence much less than that needed for the irreversible evaporation of large volumes of solvent.

The pyrolysis of potassium carbonate (reaction 30) has been investigated in detail[30]. The reaction follows the rate law

$$kt = 1 - (1-\alpha)^{1/3} \qquad (33)$$

where α is the fraction of material reacted. According to the authors it could, with an initial half life of about 4 min at 490°K, be driven by the exothermicity of the hydrogen iodide/mercury reaction.

At 600-700°K reaction 31 essentially follows equation 34. The pathway involved can be represented by the rate law:

$$d\left(HgI_2\right)/dt = k\cdot(HI)^2\cdot(NH_3) \qquad (34)$$

Over the temperature range 570-725°K, k is given by

$$k = 290 \exp (+ 3250/T) \ l^3 \ mol^{-3} \ sec^{-1}$$

Thus mercury vapour at 1 atm will react with the stoichimetric quantity of ammonium iodide to ca. 90 % completion in about 3 minutes.

Crude ammonium iodide obtained from reaction 1 could also be employed in this reaction without interfering with products and yields.

Reaction 4 is essentially quantitatively complete in a few minutes when HgI_2 is passed through K_2CO_3/KI melts at ca. 1000°K.

3.5.3. Flow sheeting: energy and cost estimates

The combination of the four reactions and the introduction of procedures for the separation of products has led Appelmann et al.[29] to the designation of 26 different individual operations in a flow sheet representation of the process. This latter has allowed an evaluation of the inventory and movement of materials through the process and of its energy requirements. The authors calculate a total input of primary heat to be 730 MW and an overall thermal efficiency of about 34 %.

The primary heat is not absorbed at one constant high temperature but rather ∿21 % at 1000°K, ∿8 % at 882°K, ∿7 % at 821°K and ∿32 % at 811°K. The remainder will be required at around 600°K to operate the vapour compression stage necessary for solvent cycling. Since, at the moment, data on the hold up times of the various species in each stage are incomplete, estimates on the inventory and cost of chemicals can only be approximate. Appelman et al.[29] assuming a residence time of 200 sec in each stage arrive at the following inventory:

150 tons NH_3, 200 tons CO_2, 5500 tons isopropanol, 1500 tons KI, 1000 tons Hg, for a plant producing 874.6 moles H_2/sec (∿7x10^6 lts/hr).

The total cost of the chemical inventory (1978 prices) would be ∿M$ 21 a small fraction of the cost of the reactor providing the necessary heat (M$ 520).

4. Comparison of costs of various alternative processes for hydrogen
   production

Table 2 shows a comparison of hydrogen cost for various suggested production
methods[32].
Most of the hydrogen currently consumed is produced by catalytic steam
reforming of natural gas, thus its cost varies directly with the cost of
the latter. Hydrogen costs · of $ 1.40-1.50/10^6 BTU are usual for a natural
gas price of $ 0.50-0.60/10^6 BTU. Should the natural gas price rise to
$ 1.00/10^6 BTU hydrogen would then cost ca. $ 2.50/10^6 BTU[31]. This is then
the lower price with which alternative production technologies will have
to compete.
From Table 2 it is clear that none of the alternative hydrogen production
schemes proposed there can compete in the near-term with hydrogen produced
for $ 2.50/10^6 BTU. It is only in the long term, that is after price
increases on fossil raw materials have occured, that schemes using water as
raw material can be expected to achieve a significant share of the market.

5. Summary

The current state-of-the art in the field of thermochemical and hybrid
hydrogen production methods has been surveyed. After a long period (ca.
1970-1975) of largely computer aided generation of thermodynamically
feasible cycles R and D work has now largely centred on objective
laboratory evaluation of individual reaction steps in candidate cycles.
At this time the Westinghouse, Mark 13 and Mark 16 cycles are at once
the most intensively researched and promising of those discussed above.
Of the three the Westinghouse process by virtue of the minimal separation
work and consequent lower plant capital costs would seem to be preferred,
provided of course   cell voltages lower than these employed in conventional
electrolysis can actually be achieved. Lower cost hydrogen is expected,
although the electrolysis step will be more capital intensive.
The remaining processes still suffer from such difficult separation and
material problems that it is difficult to imagine them able to produce
hydrogen at an economically viable price in the near future.
It seems apparent to this author that considerably more research must be
directed not only towards improvements in the three major cycles discussed
above but also in the development and testing of new, as yet untried cyles.

Table 1: Some proposed thermochemical water splitting cycles

Cycle Number	Maximum Temperatures °K	Cycle	Reference
1 (a)	1100	$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2$ $Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O$ $2FeCl_3 = 2FeCl_2 + Cl_2$ $Cl_2 + H_2O = 2HCl + 1/2O_2$	34, 35
2 (b)	1300	$SO_2 + H_2O = H_2SO_4 + H_2$ (h) $H_2SO_4 = H_2O + SO_2 + 1/2O_2$	21
3 (c)	1300	$I_2 + SO_2 + H_2O \quad H_2SO_4 + 2HJ$ $2HJ = H_2 + J_2$ $H_2SO_4 = H_2O + SO_2 + 1/2O_2$	9a,b
4 (d)	1100	$Br_2 + SO_2 + H_2O \quad H_2SO_4 + 2HBr$ $2HBr = H_2 + Br_2$ $H_2SO_4 = H_2O + SO_2 + 1/2O_2$	16, 17
5	1200	$SO_2 + H_2O + CH_3OH = CH_4 + H_2SO_4$ $CH_4 + H_2O = CO + 3H_2$ $H_2SO_4 = H_2O + SO_2 + 1/2O_2$ $CO + 2H_2 = CH_3OH$	
6 (a)	1100	$2ZnO + Se + SO_2 = ZnSe + ZnSO_4$ $ZnSe + 2HCl = ZnCl_2 + H_2Se$ $ZnCl_2 + H_2O = ZnO + 2HCl$ $ZnSO_4 = ZnO + SO_2 + 1/2O_2$ $H_2Se = H_2 + Se$	25a,b,c
7	----	$2CeO_2 + 8HCl = 2CeCl_3 + 4H_2O + Cl_2$ $2CeCl_3 + 2H_2O = 2CeOCl + 4HCl$ $2CeOCl + 2H_2O = 2CeO_2 + 2HCl + H_2$ $Cl_2 + H_2O = 2HCl + 1/2O_2$	36
8 (e)	650	$CaBr_2 + H_2O = CaO + 2HBr$ $CaO + Br_2 = CaBr_2 + 1/2O_2$ $Fe_3O_4 + 8HBr = FeBr_2 + 2FeBr_3 + 4H_2O$ $2FeBr_3 = 2FeBr_2 + Br_2$ $3FeBr_2 + 4H_2O = Fe_3O_4 + 6HBr + H_2$	37
9 (f)	750	$CaBr_2 + H_2O = CaO + 2HBr$ $CaO + Br_2 = CaBr_2 + 1/2O_2$ $3FeBr_2 + 4H_2O = Fe_3O_4 + 6HBr + H_2$ $Fe_3O_4 + 8HBr = 3FeBr_2 + 4H_2O + Br_2$	37
10 (g)	1000	$2NH_3 + 2KI + 2CO_2 + 2H_2O = 2NH_4I + 2KHCO_3$ $2KHCO_3 = K_2CO_3 + CO_2 + H_2O$ $Hg + 2NH_4I = 2NH_3 + HgI_2 + H_2$ $HgI_2 + K_2CO_3 = 2KI + Hg + CO_2 + 1/2O_2$	29
11	600	$6/5MgO + 6/5I_2 = 1/5Mg(IO_3)_2 + MgI_2$ $1/5Mg(IO_3)_2 = 1/5MgO + 1/5I_2 + 1/2O_2$ $MgI_2 \cdot 6H_2O = MgO + 2HI + 5H_2O$ $2HI = H_2 + I_2$	38

(a) Many variations suggested

(b) Generally known as the Westinghouse hybrid cycle.
    In Europe Termed Ispra Mark 11

(c) Also called the General Atomic Sulfur-Iodine cycle.

(d) In Europe known as Ispra Mark 13

(e) UT2 (University of Tokyo)

(f) UT3

(g) ANL 4 (Argonne National Laboratory)

(h) an electrolytic step

Table 2: Comparison of hydrogen production costs for various processes

1) Processes based on fossil materials

Process	Capital costs ($/KW)	Hydrogen price	Reference
Reforming of natural gas	150	1.40-2.50	1
Gasification of coal	500	4.50	1
Partial oxidation of oil	---	1.80-3.50	3

2) Processes based on solar energy

Process	Capital costs ($/KW)	Hydrogen price	Reference
Solar tower	930	16.70	1
Solar driven thermo-chemical cycle	670	8.35	1
OTEC	1000	9.15	1

3) Electrolytic processes

Process	Capital costs ($/KW)	Hydrogen price ($/10^6 BTU)	Reference
conventional electrolysis	250-300	10-15 *	2
nuclear electrolysis	---	5·10	6

4) Thermochemical Cycles

Process	Capital costs ($/KW)	Hydrogen price ($/10^6 BTU)	Reference
Westinghouse hybrid sulphur cycle	---	4.90-7.66	4
LASL-study	---	4.65-11.65	5
Cox-study	100-300	2.95-5.75	7

* electricity price 20 mills/KWh (1 mill = $ 10^{-3})

** price of raw material assumed to be $ 0.80-2.40/10^6 BTU

*** projected technology (1985). Electricity available from an HTR at 13 mills/KWh

**** price of natural gas assumed to be $ 0.50-0.60/10^6 BTU

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