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THERMOCHEMICAL PROCESSES
FOR HYDROGEN PRODUCTION
BY WATER DECOMPOSITION

Progress Report

For Period
April 1, 1975 - December 31, 1975

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ABSTRACT

The interest in hydrogen as a chemical feedstock and as a possible non-polluting fuel has continued to be high, affected by recent estimates of 1980 prices for imported natural gas in the range of \$3.00/MM Btu.

Our exhaustive survey of multi-step thermochemical and hybrid cycles concluded that the most promising prospects to date are (1) a modification of Abraham's ANL-4 cycle, and (2) the Rohm and Haas multi-reaction, single reactor cycle. Both sequences utilize iodine-based oxidation-reduction chemistry and each ultimately produces hydrogen via an iodide vapor decomposition, in the first case from NH_4I , in the second from HI . Process feasibility depends on demonstration of separation steps of relatively low energy requirements.

Further research is proposed along four lines: (i) modeling and computation focusing on selectivity in gas-solid reactions, (ii) experimental studies of solids flow and mixing, as well as mass transfer and chemical reaction in rotating and/or oscillating kiln reactors, (iii) kinetics of the crucial reactions in the ANL-4 and Rohm and Haas cycles, and gas separations associated with these processes, and (iv) flow sheet evaluations and preliminary economics.

THERMOCHEMICAL PROCESSES FOR HYDROGEN PRODUCTION BY WATER DECOMPOSITION

INTRODUCTION

The interest in hydrogen as a chemical feedstock and as a possible non-polluting fuel has continued to be high over the seven-month period during which this research has been in progress. National meetings focussing on aspects of this technology include the First World Hydrogen Energy Conference to be held in Miami in March, 1976 and such short courses as the one entitled Hydrogen Energy scheduled for January, 1976 at the University of New Mexico.

As a chemical intermediate, hydrogen becomes increasingly valuable with the rise in natural gas price, since steam reforming of methane is still the route of choice at this time. Recent reports (A12) estimate that imported natural gas may be worth \$3.00/MM Btu or more by 1980. It is of interest in this connection to note that the natural gas consumed in the steam reforming process is about half reacted as a chemical and about half burned as a fuel. Evidently an alternative process (such as water splitting) could save an appreciable fraction of the methane used, even if it continued to use natural gas as a fuel. Another uncertainty of considerable magnitude arises from the controversy that surrounds the potential of methanol as component of motor fuel. Any growth in this market for methanol would be

reflected in a corresponding demand for hydrogen. Similarly, there are still questions on the specific demands that our emerging national energy policy will place on hydrogen for coal treatment and fuel desulfurization generally.

Specific attention to closed thermochemical cycles has been of two sorts. The more optimistic school of thought has focussed on new chemical combinations, the underlying expectation being that the known difficulties are specifically associated with known cycles and are not inherent in the idea. Bamberger and his co-workers (A1) have for example studied selected reactions of chromium and barium compounds to demonstrate the chemical feasibility of a cycle based on the reactions:

(ORNL-1)

(ORNL-2)

(ORNL-3)

The authors properly point to several very substantial advantages in this choice and suggest also that the physical separation of the various solids are not a trivial matter. The energy efficiency of this separation as well as that of the salt evaporations needed may be expected to be the crucial decision variables.

The second approach to the evaluation of closed thermochemical cycles has been to emphasize the economics of investment and operation as currently available. Shinnar (A9)

has demonstrated that the heat requirements of Wentorf and Hanneman's Process B are such as to disqualify this process from serious consideration "in the present state of the art," and has argued by inference that other suggested processes have to bear similar burdens.

It should by now be apparent that process complexity in terms of mass and heat transfer as well as physical separations are as important to cycle feasibility as is the chemistry. The discussion of current prospects and of proposed research is guided by this overview.

DISCUSSION

To up-date the state-of-the-art discussion presented in the original proposal for this project, it is necessary to consider (i) thermodynamic evaluations, (ii) chemical cycles of greatest current promise, and (iii) progress in solids handling and separations. The following is divided into three sections along these lines. It highlights progress to date and provides the bases for the proposed work to be done.

A. Thermodynamic Evaluations

An exhaustive survey of all the multi-step processes proposed (as of last Spring) showed that they can all be classified as variations on one or another of standard three-

step processes. Our thermodynamic studies based on available literature data suggest that a minimum of six reaction steps would be necessary in order that every reaction in the sequence can be carried out under not-very-unfavorable conditions. The usual first-approximation flowsheet calls for a separation or heat exchange operation for each reaction. Since each operation adds to the capital cost and contributes inefficiencies, it is difficult with such a flowsheet to picture a process involving four or more reactions that can successfully compete. This part of our work concluded that there is good reason to doubt the existence of workable thermochemical processes, unless processes are conceived of that avoided intermediate separations (A15; see Appendix 1 for preprint copy).

In an effort to allow for some of the advantages of electrolytic processing without suffering all the inefficiency of water electrolysis, a study was made of possible hybrid cycles; i.e., cycles in which one step was electrolytic, and the remainder were thermochemical. With this in mind the following additional criteria were imposed:

- (i) No more than three reactions were allowed, including the electrolysis.
- (ii) The maximum temperature allowed for a chemical reaction was 750°C.
- (iii) Chemical reactions had to be nearly irreversible, as clean as possible, and free of complicated or costly separation processes.

(iv) The electrochemical reaction had to satisfy the Gibbs free energy limits:

$$\approx 30 \leq \Delta G_e \leq \approx 35 \text{ Kcal./mole of hydrogen}$$

in order to have a significant advantage over water electrolysis, whose ΔG is about twice this value.

The most promising two-step sequences involved electrolytic reactions of water with metal oxides to produce hydrogen, followed by thermochemical regeneration to liberate oxygen, as follows:

or

These oxide thermal decompositions require temperatures above 750°C .

Similar problems are encountered in both systems. From research done on cobalt electrodes (A8), it is known that in basic solutions the following reactions occur at the cobalt anode:

Once the cobalt anode is covered by a $\text{Co}(\text{OH})_2\text{-CoO-Co}_3\text{O}_4$ layer the anode becomes passive, and oxygen starts to evolve (A2). The thickness of the layer will depend on the current density, the shape of the electrode, and the degree of agitation of the electrolyte. The possible reactions of a copper anode in a basic solution are:

It has been demonstrated that oxygen starts to evolve at the anode (A4) when the $\text{CuO-Cu}(\text{OH})_2$ layer is only a few molecules thick. Unfortunately, these reports indicate that neither of these electrolytic reactions can be carried out on an industrially satisfactory scale.

A possible alternative for electrolysis is the high temperature ($\sim 1000^\circ\text{C}$) reaction

if it were coupled with

but aside from the gas separation required on the products, there is no satisfactory way to carry out practical gas electrolysis. Dozens of other combinations were examined for hybrid sequences at various levels of complexity. In most cases, there was no evidence available in the literature

that the electrochemical reaction in question was able to be carried out. Others presented troublesome side reactions, kinetics problems, or difficult separations. In the end no acceptable hybrid process based on known data could be found. A first draft report on these studies is attached as Appendix 2.

B. Chemical Cycles

There can be no question that the movement in the evaluation of specific proposed thermochemical cycles has been in the direction of elimination of candidates, rather than expansion of the range of choice. The critics have performed an invaluable service in focussing on the many economic, operational, and safety problems. These objections notwithstanding, there are still prospects that may provide economic hydrogen within constraints of feasible large scale production. Each of these is supported by demonstrated laboratory chemistry, and each in turn is still built on detailed separations or reactor design of some uncertainty.

1. Abraham's ANL-4 Cycle:

The first formulation of the ANL-4 cycle was communicated by Abraham in an Information Memorandum (BMA/FDS 75-VII-7-1) as the sequence:

Abraham pointed out that (R41) is a modification of the Solvay process used for the commercial production of NaHCO_3 :

for which:

$$\Delta G^\circ = -10.24 \text{ Kcal}$$

$$\Delta H^\circ = -54.86 \text{ Kcal}$$

$$\Delta S^\circ = -149.73 \text{ e.u.}$$

It should therefore be expected that the reaction (R41) will proceed in a similar way, and standard texts such as Shreve (A10) indeed confirm this, but do suggest that extensive separation equipment would be called for. The reaction (R42) is known and generally straightforward. Any chemical uncertainties associated with the two final reactions (R43) and (R44) have been resolved in Abraham's laboratory, where excellent yields (>95%) were demonstrated at temperatures of about 750°K and 900°K, respectively.

Further details on energy and separation needs can be shown by interpolating the physical steps between the chemical reactions given to show the sequence as:

This formulation of the cycle is instructive in that it emphasizes that unless some way of extracting NH_4I from aqueous solution can be found, the heat requirements will be quite high for the drying of NH_4I , steps (R4a) and (R4b). These solutions tend to decompose in the presence of air and the rate is increased by intense light. Further separation problems may be encountered in handling the NH_3/H_2 and CO_2/O_2 gas mixtures produced in (R-43) and (R-44), respectively. Pertinent thermodynamic values for these reactions are given in Table 1.

The use of mercury in reactions (R43) and (R44) is an obvious drawback to the ANL-4 sequence. Abraham recognized this when he first proposed the NH_4I -based cycle at the April, 1975 ERDA meeting in Germantown. His original intention was to examine the cycle:

which is free of mercury; however, there was doubt as to whether reaction (R46) was selective enough in competition with the formation-decomposition of HI. Since that time Kittle (A11) has reported experimental evidence for the

TABLE 1
THERMODYNAMIC VALUES FOR
REACTIONS IN ANL-4 SEQUENCE

<u>STEP</u>	<u>ΔG°</u>	<u>ΔH°</u>	<u>ΔS°</u>
R41	-6.60	-54.72	-160.5
R42	7.02	32.82	86.58
R4a	8.80	-6.56	-51.54
R4b	--	80.56	--
R43	--	--	--
R44	29.10	42.02	43.36
R4c	-3.57	9.80	44.84
R4d	-2.06	-10.52	-28.39

ΔG° and ΔH° are in Kcal/mole H_2

ΔS° is in e.u./mole H_2

Data from the National Bureau of Standards Thermodynamic Tables.

catalytic vapor phase reaction (R46), making this modification of Abraham's cycle one of the most attractive candidates to date.

2. The Rohm and Haas Cycle:

In a paper submitted to the First World Hydrogen Energy Conference to be held in Miami next March, Kittle and his co-workers (A5) consider the sequence:

but, since HIO is believed to have only a very short lifetime, the first two reactions are combined to give

Among these reactions, a question of chemical feasibility only exists for (RH5), since the decompositions of HI and of HIO_3 are well documented in the literature (A13, A14).

The Rohm and Haas report leaves no doubt that the products of (RH5) are being identified chemically in significant yields, in spite of the unfavorable equilibrium constant for this reaction. Evidently the reaction is being shifted to the right by the rapid removal of the solid HIO_3 , or perhaps as Kittle suggests by "the generation of an intermediate solid phase."

In view of the hard experimental support, this sequence must be considered a prime contender, especially because it

lends itself to an extremely compact process design, apparently free of complex separations and aided by a simple and direct recycle of partially-converted feed. In Kittle's words:

"The three-step iodine reaction sequence lends itself nicely to a continuous process. The feedstream containing iodine and water can be admitted to the first reactor unit where reaction (5) occurs, leaving iodic acid behind. The effluent, hydrogen iodide and unreacted starting materials, then enters a second stage, where the HI is converted to H_2 and I_2 , with the iodine being recycled, and the hydrogen dried and collected. Intermittently, the first reactor unit can be heated, to decompose the iodic acid, yielding iodine, water and oxygen. Many variations of this reactor staging can be used depending upon timing."

C. Reactions of Solids

Studies are in progress on several aspects of solids processing that are crucial to the design of gas-solids reactors such as will be needed for hydrogen-producing sequences. The results of these analyses and experiments will be useful for implementing Abraham's cycle, the Rohm and Haas cycle, or any of the many others that have been proposed.

1. Selectivity in Gas-Solid Reactions:

Several models for gas-solid reactions have been discussed in the literature under the rubrics of shrinking core, porous pellet, and structured models. The results are valid for single reactions, but do not account for complex situations that include the presence of multiple reactants in the feed or sequential reaction of the products with the

reactant solid. In systems such as the gasification of coal, reduction of iron ore, or the fluorination of uranium, the presence of simultaneous reactions can cause striking changes in the overall rate and the selectivity for any one reaction.

Our preliminary results for isothermal, independent gas solid reactions of the type

predict a maximum in the selectivity for one reaction over the other as solid conversion increases. Numerical results can differ by as much as an order of magnitude depending on whether structural or shrinking core models are used. This suggests that it may be advantageous to carry out certain reactions by precompressing non-porous particles into larger porous networks. The reduction in rate accompanying such a step may in some cases be justified by the improvement in product quality as a result of higher selectivity.

In the case of non-porous particles the selectivity is also seen to be very sensitive to temperature changes. The structural model predicts a temperature range in which the selectivity goes through a local maximum and a local minimum. In this range the selectivity change is gradual, suggesting that the selectivity might be easier to control if non-porous particles were compressed into porous pellets.

2. Structural Kinetic Models

Structural models are those that attempt to account for non-homogeneities in solids in terms of some particle substructure. One of the shortcomings of the structural models presented in the literature is their failure to predict the initial stage of reaction during which the reaction rate rises to a maximum with increasing conversion. It appears that the initial stage of reaction may be characterized as one in which the surface area available for reaction is increasing. It is probable that this increase is due to an activated initiation step on the surface of the grains with an inherent activation energy different from that of the desired chemical reaction. Such a hypothesis was proposed by Avrami (B20) and later demonstrated to fit experimental data for solid decomposition reactions.

If indeed such an activation step exists for gas-solid reactions, the maximum in the reaction rate would be expected and the new picture would be a more precise explanation for the mechanism of gas-solid reactions. This can only be verified by solving the equations describing the process and comparing the calculations with experimental data. The results would need to be reconciled with earlier work. Hills (C2) used a sharp interface model to describe the thermal decomposition of calcium carbonate. Sugiyama and Hasatani (C4) found that a porous pellet model was suitable in representing the decomposition of gypsum. Sugiyama and Kito (C5) have applied three different models to the decompo-

sition of sodium bicarbonate and compared the predicted rates with experimental observation. Campbell et al. (C1) have described the use of a porous lime sphere in determining the diffusivity of CO_2 in regard to the thermal decomposition of CaCO_3 . In another study Satterfield and Feakes (C3) compressed dry CaCO_3 around a thermocouple which was then inserted axially in a tubular furnace.

3. Moving Bed Reactors

Moving bed reactors find application in the chemical and metallurgical industry in a wide variety of processes, among them the all-important blast furnace reduction of iron ore. In spite of their apparent simple geometry such reactors are usually difficult to model without simplifying assumptions since very little is known about the motion of solid particles in these reactors, and the thermal transport properties of solid particle beds have not yet been characterized in sufficient detail. In some cases it is nevertheless possible to build models that fit experimental data within acceptable limits. (D1-D12). Ishida and Wen (D5) have presented a steady state analysis in which the motion of the solid particles was considered to follow a plug flow pattern. The effect of radial dispersion was accounted for in the analysis of Lahiri and Seshadri (D6), and was analyzed for fixed beds by De Wash and Froment (D3). Schaefer et al. (D8) analyzed the steady-state behavior of a moving bed reactor for the case of fast chemical reaction with a step increase in heat generation rate at the ignition temperature. An important

aspect of moving bed reactors which has been tacitly neglected in the analyses of Schaefer et al. and of Ishida and Wen is that of gas flow and pressure in the bed. In their analysis of the blast furnace process, Lahiri and Seshadri (D6) used the Ergun equation for fixed beds (D4), but the same equation was later shown to be better for moving beds after some modification in the gas velocity parameter (D12).

4. Rotary Kiln Reactors

Rotating dryers, mixers, grinders and heaters are well known in the process industries (B1-B17). They are also used for chemicals in calcining of limestone for cement, in the production of Al_2O_3 from basic salts, and for roasting pyrites in sulfuric acid preparation. The advantages of this reactor type are in the freshly-renewed well-mixed solid that moves longitudinally through the reaction zone at a steady rate. The firing time is relatively short and it is well-suited to handling very fine grains without overload even at extreme temperatures.

The movement of solids in a rotating kiln has been extensively studied and three conditions of particle movement have been defined: cascading, cataracting, and centrifuging (B12). At low rotational speeds the particles travel in circular arcs concentric with the shell of the mill until a point of instability is reached, after which they roll down the particle surface. The latter condition is defined as cascading (B6, B13, B17). At higher rotational speeds the outer particles are projected into space and

describe approximately parabolic paths. This is called cataracting. At still greater speeds the paths of the particles coincide with the circumference of the kiln. The particle is then said to be centrifuging. The analysis of rotary kiln reactors is complex because of the difficulty in describing the motion of solid particles in the rotary bed.

Studies on the mixing of solid particles in rotating drums have been conducted by Carley-Macaulay and Donald (D2). The results dwell upon aggregate mixing behavior with application to the calculation of mixing indices, but what is needed for design is the characterization of the motion of individual particles. Attempts have also been made to fit a diffusive mechanism to the movement of solid particles to compare predicted residence time distributions with experimental measurements. Fan and Ahn (B18) used the impulse response data of Miskell and Marshall (D7) to determine the diffusivity of solid particles, neglecting the change in flow cross-section with axial position in the kiln. Ryvkin et al. (B19) found that the residence time distribution of solids in longitudinal flow in a rotating furnace agreed with predictions from theory using a diffusive mechanism. Further experimental confirmation is necessary before application is possible.

In spite of the difficulties in describing the motion of solids, studies using elementary models have been reasonably successful in qualitatively describing the phenomena occurring in a rotary kiln. Spang (D10) analyzed the dynamic

behavior of a cement kiln, and in another work Manitus et al.(B7) described a mathematical model for an aluminium oxide rotary kiln. Plug flow of solids was assumed in both these models; the treatment cannot be refined to produce more accurate results unless the heat and mass transfer effects are individually studied in detail.

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APPENDIX 1

PAPER ON HYDROGEN PRODUCTION FROM WATER
BY MEANS OF CHEMICAL CYCLES

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HYDROGEN PRODUCTION FROM WATER
BY MEANS OF CHEMICAL CYCLES

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ABSTRACT

A thermochemical process uses heat instead of work to dissociate water into hydrogen and oxygen. The principle by which a reaction with an unfavorable ΔG can be driven by dividing it into several steps is discussed. Dozens of cycles that operate below 800°C have been proposed but none of them has been shown to work. Previous research indicates that no two-step cycle exists. A systematic study of three-step processes was performed by classifying them into standard patterns. The result of the study is that a three-step cycle probably does not exist.

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INTRODUCTION

The importance of hydrogen as a potential non-polluting fuel is well-known. It will however be in short supply sooner as a chemical feedstock, since hydrogen is the basic raw material and major cost for fertilizer via nitrogen fixation by the Haber process, the crucial ingredient in coal liquefaction and petroleum desulfurization, as well as the limiting reactant in methanol synthesis for solvent uses and possible substitution for gasoline or liquid fuels.

With these needs in mind, it is clear that new non-fossil sources of hydrogen should be studied, whatever the controversy about the role of hydrogen in a "hydrogen fuel economy" of the future. A closed-cycle thermochemical process is designed to split water into hydrogen and oxygen using only water and heat energy (at less than 800°C) but no other raw materials. The advantage over electrolysis is the potentially higher thermal efficiency (perhaps 50%) associated with the thermochemical method.

Key references which contain the most important thermochemical processes proposed to date can be found in six recent papers (Abraham and Schreiner, 1974; Chao, 1974; Euratom, 1973; I.G.T., 1972; Russell and Porter, 1974; Wentorf and Hanneman, 1973). Most of these processes appear to be unfeasible. Untested new processes continue to be proposed. The purpose of this work is to attempt to generate new processes in a systematic way, as a step toward identifying the optimum process.

Any attempt to generate new processes and to determine the minimum number of reaction steps requires insight into the principles by which unfavorable reactions can be driven by heat instead of work.

THERMODYNAMIC CONSIDERATIONS

Overcoming the free energy barrier

The basis for comparing a thermochemical process for production of hydrogen with electrolysis is efficiency. Thermal efficiency is defined as the ratio of energy output (electrical or chemical) to energy input.

The overall thermal efficiency for converting heat to chemical energy by electrolysis is less than 30% in the 1970's and can eventually be raised to about 40% (I.G.T., 1972). A major breakthrough toward production of cheaper hydrogen must be associated with the avoidance of power generation. A thermochemical process attempts to achieve such a situation. Its maximum thermal efficiency is about 87% if it is driven by a heat source at 800°C. The actual efficiency will be a function of irreversibilities in chemical reactions, separations, heat exchange, etc. but cycles with values greater than 40% can be regarded as promising.

For the water-splitting reaction:

standard thermochemical data at 25°C are

$$\Delta G = 56.69 \text{ kcal}$$

$$\Delta H = 68.32 \text{ kcal}$$

$$\Delta S = 39.01 \text{ cal/}^\circ\text{K}$$

Since the reaction is endoergic, it cannot be carried out at 25°C without performance of at least 56.69 kcal of work per mole of hydrogen. There is only one way to avoid the supply of work: coupling of the desired reaction to another that has a larger decrease in free energy so that the overall set of coupled reactions shows a decrease. This is the mechanism by which many endoergic biological reactions take place but it is certainly not applicable to production of non-fossil fuels.

There are three ways of supplying the work. The first one is electrolysis work and it is to be avoided. Another means of overcoming the positive free-energy barrier is by mechanical P-V work. For a gaseous reaction the equilibrium constant for mole fractions (K_y) depends upon the pressure according to the approximate equation:

$$\ln K_y = -(\sum v_i) \ln P - \frac{\Delta G}{RT} \quad (1)$$

where $(\sum v_i)$ is the summation of stoichiometric coefficients (products less reactants). If ΔG is large and positive and K_y is small, it can be increased to a value of unity by adjusting the pressure to:

$$P = \exp \left[\frac{-\Delta G}{RT(\sum v_i)} \right] \quad (2)$$

Since pressure varies exponentially with ΔG , rather extreme values of pressure are needed to overcome values of ΔG larger than a few kcal. The rule-of-thumb that ΔG should not exceed 5-10 kcal applies here. Besides, P-V work requires electrical power generation and would offer no advantage over electrolysis.

Instead of driving the reaction to the right by pressure, one can force

an unfavorable reaction to completion by separation work and recycling. Even if the reaction has favorable kinetics and a clean separation process (e.g. membrane) can be devised, one cannot avoid the fact that ΔG is the minimum separation work. The rule-of-thumb that ΔG at the reaction temperature should not exceed 5 to 10 kcal also applies here because separation work is notoriously inefficient, particularly at low values of concentration. For example, the efficiency ($\Delta G/W$) of water desalination by the best reverse-osmosis process is less than 20%. Therefore it is extremely unlikely that a water-splitting process driven mainly by separation work can compete with electrolysis.

Reaction Splitting

The third and most versatile method is producing the work inside the system, using heat from the heat source. The amount of heat needed will, of course, be larger than the required work according to Carnot's limitation:

$$Q_H \geq W \left(\frac{T_H}{T_H - T_C} \right) \quad (3)$$

The chemically-reacting system also works like a heat engine whose potential work output is applied directly to overcome the free energy increase. Heat-driven separation processes would fall under this description but we know that separation work is very inefficient. The heat should instead be supplied to one or more endothermic reactions, not necessarily the one we are interested in. It will be seen that a set of both endothermic and exothermic reactions can also perform as a heat engine.

A reaction such as water-splitting which is endothermic and endoergic can be carried out without work at a higher temperature where $\Delta G = 0$.

The dependence of ΔG on temperature is

$$\frac{d\Delta G}{dT} = -\Delta S \quad (4)$$

Very often, as in the case of water-splitting, the ratio $\Delta G_{298}^{\circ} / \Delta S_{298}^{\circ}$ is so large that an extremely high temperature is needed to achieve a condition of negative or even slightly positive ΔG . If it is desired to operate under conditions of negative or slightly positive ΔG , a last resort is to divide the desired reaction into several steps among which the overall ΔG_{298}° and ΔS_{298}° are unevenly distributed. A good example of this technique is found in the dissociation of hydrogen iodide:

This reaction shows a positive ΔG_{298} and the work requirement increases with temperature, at least initially, because ΔS_{298}° is negative. But if it is split into:

and

then the first step occurs spontaneously. The second step looks less favorable than the original reaction but it has a large positive ΔS at 298°K so that ΔG decreases more rapidly with temperature and vanishes at 950°C.

Use of this technique of splitting a reaction into steps with unequal entropy distribution implies the inclusion of one or more exothermic reaction steps. Otherwise if the overall reaction is divided into several

endothermic steps, the improvement in equilibrium yield in one of them must be achieved at the expense of worsening the yield for another.

In that case reaction splitting does not represent an improvement but a disadvantage. It should also be expected that costs increase very rapidly with the number of steps. Only when the splitting is into both exothermic and endothermic steps can the work requirement be reduced and eventually be made to vanish by a proper choice of reactions and temperatures. If the use of external work (electrical, P-V or separation work) is to be avoided then the inclusion of exothermic steps is an obvious second law requirement.

Target Processes

Let us assume that all the endothermic reactions are carried out at T_H and all the exothermic ones at T_C . The thermal efficiency is then

$$\eta \leq \frac{\Delta H_{298}}{\Delta G_{298}} \left[\frac{T_H - T_C}{T_H} \right] \quad (5)$$

where ΔH_{298} and ΔG_{298} are 68.32 kcal and 56.69 kcal respectively. For $T_H = 800^\circ\text{C}$ and $T_C = 25^\circ\text{C}$ the constraint is $\eta \leq 0.87$. Selection of 800°C for the temperature of the heat source is based upon the next generation of nuclear reactors, the high temperature gas cooled reactor.

It follows from our assumption that we can collapse all the endothermic reactions together and do the same with the exothermic ones, thus leaving a hypothetical two-step cycle. Let the superscript I denote the quantities associated with its high-temperature step. As this step will probably be strongly endoergic the temperature increase is the means to bring its ΔG^I ,

and therefore the work requirement, down to zero or even negative values. This situation is achieved at a certain T_H which is the solution of

$$\Delta G^I = \Delta G_{298}^I + (\Delta C_p^I - \Delta S_{298}^I) (T_H - 298) - \Delta C_p^I T_H \ln \left(\frac{T_H}{298} \right) = 0 \quad (6)$$

where ΔC_p^I must be an average in the interval $(298, T_H)$. We can obtain an order-of-magnitude estimate of this T_H by setting $\Delta C_p^I = 0$.

Then

$$T_H \approx \frac{\Delta H_{298}^I}{\Delta S_{298}^I} \quad \text{for } \Delta G^I = 0 \quad (7)$$

If ΔC_p^I is positive this value represents an upper bound. As T_H is limited by technological reasons to about 800°C this is actually a relation between ΔH_{298}^I and ΔS_{298}^I , for the endothermic reactions as a whole.

But there are more specific restrictions on their particular values. If the chemical engine is to provide the 56.69 kcal of work, then by the first law of thermodynamics this quantity also represents the minimum heat to be provided by the source. If, as before, $\Delta C_p^I \approx 0$ then

$$\Delta H_{298}^I > 56.69 \text{ kcal} \quad (8)$$

By the second law of thermodynamics, if no external work is supplied:

$$\frac{\Delta G_{298}^I}{\Delta H_{298}^I} < \frac{T_H - T_c}{T_H} \quad (9)$$

where $\Delta G_{298}^I = 56.69 \text{ kcal}$. In the reversible case the equality holds.

If T_H is taken as 800°C it follows from equations (7) and (9) that

$$\begin{aligned}\Delta H_{298}^I &\geq 78.50 \text{ kcal} \\ \Delta G_{298}^I &\geq 56.69 \text{ kcal} \\ \Delta S_{298}^I &\geq 73.15 \text{ eu}\end{aligned}\tag{10}$$

The condition $\Delta G_{298}^I \geq 56.69 \text{ kcal}$ implies $\Delta G_{298}^{II} \leq 0$ so that the low temperature exothermic reactions, taken as a whole, will proceed spontaneously.

Several hypothetical two-step processes are listed in Table 1. They are hypothetical in the sense that reactions I and II must sum to the dissociation of water and such combinations may not exist. However, an examination of the table leads to several interesting conclusions. Consider process A, which is the ideal, reversible case ($K=1$). The endothermic reactions require a ΔS_{298} of 73.15 eu. But there are very few inorganic chemical reactions with $|\Delta S|$ larger than 30 or 40 eu per mole of equivalent hydrogen, with 20 eu being a more typical value. We could hope for a three-step process composed of two endothermic reactions and one exothermic reaction but the requirement that all three steps have large $|\Delta S|$ and the additional restriction that they must sum to the dissociation of water makes the existence of the combination unlikely. Therefore a practical thermochemical process operated by a heat source at 800°C will probably be composed of four or five reactions. This conclusion is supported by the processes that have been discovered so far.

Pattern processes B and C are also chemically reversible. They improve the yield of one reaction ($K=100$) at the expense of the other

($K=0.01$). Ideally these processes would show the same efficiency value as A, i.e. 0.87. But this table also takes into account the low efficiency of the separation work that must be associated with a K of 0.01. Separation energy is taken as $\Delta G/\eta$ with $\eta=0.1$. Other losses in efficiency due to pumping work, heat exchange, etc. are not included. Processes B and C show that separation work associated with unfavorable yields ($K<1$) lowers the efficiency drastically, particularly at high temperature. On the other hand, pattern processes D and E show that the penalty in efficiency for chemical irreversibility ($K>1$) is not too large but the high values of $|\Delta S|$ imply an increase in the number of steps. For example, a process of type D would require at least 5 and possibly 6 separate reactions.

Table 1 shows that the reaction equilibria must lie to the right in order to avoid costly separation work. It is unlikely that all of the exothermic reactions can be run at 25°C because of kinetic limitations, so they must be quite irreversible at 25°C if the equilibrium is to be favorable at an intermediate temperature (say, 300°C). The efficiency based upon chemical irreversibilities cannot be much less than 60% if the process is to be competitive with electrolysis; otherwise the actual thermal efficiency will be less than the target value of 50%. Therefore it is our opinion that a successful thermochemical process must fit the pattern of process F. This knowledge is extremely useful for the evaluation of proposed processes.

Thermodynamics provides a very convenient frame of reference in

which to pose the problem of the search for viable processes. It also imposes rather severe constraints that greatly reduce the number of options to be examined. But there are other necessary conditions that have to be met simultaneously.

The first and most obvious requirement is closure, i.e. that all reactions must add to water decomposition, everything else being recycled. Closure is best dealt with by using closed standard patterns. Each pattern represents a certain way of decomposing water in a given number of steps, by generalized reagents. Building a cycle thus means specifying those reagents, in a manner compatible with the thermodynamic constraints. Standard patterns for two and three-step processes are shown in Figures 1 and 2.

The kinetics, although of primary importance, do not provide a basis for a systematic search. The logical sequence is to first establish thermodynamic feasibility and then study kinetic behavior. Known chemical reactions which have already been run on an industrial scale are obviously desirable.

Nearly complete recovery is an essential feature of a viable closed cycle process, especially in a case like water splitting that would involve a very large scale of operation. Side reactions are unwanted; they can be accepted if unavoidable and if their products can be recycled but this represents a toll on the efficiency.

TWO STEP PROCESSES

Funk and Reinstrom (1966) have shown in an early work that no two-step

reaction sequence exists that can operate within practical temperature limits. It seems of great value to determine which two-step process comes closest to realization from the thermodynamic point of view. This procedure will prove itself useful in the development of multi-step cycles.

There are two different schemes for two-step processes, as shown in Figure 1. Funk and Reinstrom named them "oxide" and "hydride" processes, according to the nature of the intermediate.

In our nomenclature M and X simply denote elements or compounds capable of undergoing the proposed reactions, i.e. of acting as oxygen or hydrogen acceptors. No assumption is made regarding their composition or valence. As an example M may represent a metal, a lower oxide, an anion such as NO_2^- , etc.

We have already seen that if the process is going to work as a chemical engine one reaction must be endothermic and the other exothermic. The second reaction in either of the two schemes- a decomposition- has a positive change in entropy. This one should therefore be the high-temperature endothermic step.

When a specific reaction system is chosen, then the values of ΔH_{298}^I , ΔG_{298}^I , and ΔS_{298}^I are determined, and Equations (7) and (9) can be written as

$$T_H > \frac{\Delta H_{298}^I}{\Delta S_{298}^I} \quad (11)$$

and

$$T_H \geq T_C \left(\frac{\Delta H_{298}^I}{\Delta H_{298}^I - \Delta G_{298}^I} \right) \quad (12)$$

or actually

$$T_H = \max \left[\frac{\Delta H_{298}^I}{\Delta S_{298}^I}, T_C \left(\frac{\Delta H_{298}^I}{\Delta H_{298}^I - 56.69} \right) \right] \quad (13)$$

Eqn. (13) allows us to estimate how far or close any two-step sequence is from realization from the point of view of thermodynamics. Efficiency has no significance as long as the range of practical working temperatures is exceeded.

Oxide Schemes

The restriction $\Delta H_{298}^I > 56.69$ kcal rules out the use of several M-MO couples: all noble metals, several oxide-peroxide systems, mercury, selenium, tellurium, iodine, etc., but the elements and lower oxides that satisfy the inequality are still numerous.

Our goal is to find two-step sequences for which the minimum T_H , as given by Equation (13), is of the order of 800°C or less. Table No. 2 shows the results for a few of the 100 or so M-MO systems that we considered.

From such a search it can be concluded that no two-step process can be built from these systems. The optimum, i. e. the one that can be run at the lowest temperature is found to be

Consistent with this finding is the fact that this process was one of the first to be proposed (Miller and Jaffe, 1970).

Actually the chemistry of cesium is more complicated and the process involves four steps:

The only other process of this kind that could be found in the literature is a tin oxide scheme (Souriau, 1972), which actually consists of three steps:

For both the cesium and tin oxide cycles, far too high a temperature is required.

A group of potential processes that would fall under the oxide-type classification is based on the decomposition of salts of oxyacids, notably sulfates, which often has to be carried out in two steps. A generic example would be:

A certain number of sulfates have desirable thermodynamic properties such as a large entropy increase associated with the evolution of one molecule of SO_3 . Zinc sulfate appears to be the optimum. However there are serious impracticalities due to the slow kinetics of the first step. The need for an inexpensive method of separation of SO_2 and O_2 avoiding re-oxidation of the former is another obstacle.

Hydride Schemes

If the search for hydrogen-acceptors is limited to elements, then it is greatly simplified by Equation (8), which rules out almost all of them with the exception of fluorine. Chlorine also comes close to meeting the requirement.

A comparison of the second reaction in each of these possible cases with the direct decomposition of water is presented in Table 3, which shows that HF is far more difficult to decompose than water. On the other hand, HCl shows a lower ΔG° of decomposition than water but the value is still

very large and its entropy change is less favorable. No two-step hydride process can be built using an element.

SEARCH FOR A THREE-STEP PROCESS

There have been attempts to classify processes by the number of steps (Soliman et al., 1975) but three-step processes have never been studied in a systematic way.

The number of cycles to be considered increases tremendously as we go from the two to the three-step processes. We will limit our analysis to the simplest case, the one involving the least possible number of elements. This number is four, appearing in seven different molecular species. Actually the number of elements could be larger provided that the rank of the atom matrix were still three, i.e. that any extra element appeared in the same group or radical throughout the process.

Seven different kinds of three-step patterns are shown in Figure 2. M and N denote oxygen acceptor groups, as before, and X and Y are hydrogen acceptor groups. This classification shows only the simplest and most promising cases and is not meant to be exhaustive. From Figure 2 it can be noted that each pattern shows at least one reaction in which only one of the groups (e.g. M or X) is involved. That step then serves as the basis for a first screening, after which all possible second groups are examined.

Very few three-step processes have been proposed and all of them fit into one of these categories. Furthermore many cycles of four or more steps can be regarded as extensions of three-step patterns.

Type 1 Processes

The net result of the first reaction is the substitution of the problem of decomposing H_2O by the problem of decomposing HX . This task is carried out in the last two reactions in a manner analogous to the two-step oxide schemes for water splitting.

A five-step process that can be regarded as an extension and a good example of this group of cycles is the Beulah process (Wentorf and Hanneman, 1973).

which can be simplified by condensing the indicated reactions:

The first reaction (a) is the key step since only one of the two necessary reagents enters there. It can be shown (Hardy-Grena, 1973), that Cl_2 is the only element that will react with water to free oxygen in a nearly reversible manner. Fluorine is another possibility but the reaction is too irreversible and, as a result, HF is extremely difficult to decompose. Therefore all processes in this group must begin with the following endothermic reaction:

This is a well-known catalytic reaction. Its reverse is the Deacon process and it has been perfected in recent years in order to recycle large amounts of HCl that appear as by-products of the manufacture of chlorinated hydrocarbons. As indicated by Wentorf and Hanneman (1973), this reaction may be carried out in two steps, as shown in the example above, in order to avoid the high temperatures that are necessary to favor the production of oxygen.

Reaction (c) must be a high-temperature decomposition and reaction (b) must then be a low-temperature exothermic step. Since step (a) is fixed, we have:

$$\begin{aligned} \Delta H_{298}^b + \Delta H_{298}^c &= 44.12 \text{ kcal} \\ \Delta G_{298}^b + \Delta G_{298}^c &= 45.54 \text{ kcal} \\ \Delta S_{298}^b + \Delta S_{298}^c &= -4.76 \text{ eu} \end{aligned}$$

Since in general chlorides are more volatile than metals, product separation looks easier in reaction (c) than in reaction (b). In addition reaction (c) is a high-temperature one and thus it seems reasonable that it will be responsible for the largest portion of the remaining 45.54 kcal in the ΔG 's. In principle we may assume that ΔG_{298}^b will be negative or that, if it is positive, it will not exceed 10 kcal. Therefore the following inequalities must hold:

$$\Delta G_{298}^c \geq 35.54 \text{ kcal} \quad (14)$$

$$\Delta S_{298}^c \geq 0 \quad (15)$$

Our aim is to find the process in which reaction (c) can be carried out at the lowest possible temperature; we can simplify such a search by locating an M that minimizes $\Delta G_{298}^c / \Delta S_{298}^c$.

We tabulated values of ΔG_{298}^c and $\Delta G/\Delta S$ at 298°K for reaction (c) for a large number of M-MCl_n pairs. M denotes a metal or a lower chloride. Table 4 is a list of several reactions that meet the above inequalities and show a relatively low ratio $\Delta G/\Delta S$. The most favorable one is the decomposition of chromium trichloride, which corresponds to the process:

This process has already been proposed by Knoche (Marchetti, 1973).

The next best cycle that shows $\Delta G_{298}^b \leq 0$ is:

There is a similar cycle with nickel replaced by cobalt. These three cycles (Cr, Co, Ni) are optimum ones for this group in the sense that they can be run at the lowest temperature. Unfortunately the temperature is still far above the target of 800 °C.

If we allow a slightly positive ΔG_{298}^b in the low temperature step then the following cycle is the next candidate:

This cycle has been proposed and tested by Funk (1972), who could not carry out the second reaction. In his process reaction (c) is split into:

The second best cycle in this category is

The last two cycles fail for the same reason: the dissociation reaction has acquired a favorable free energy change at the expense of the second reaction, which has now become unfavorable.

Type 2 Processes

The first reaction amounts to the substitution of water, regarded as an oxide, by MO. The decomposition of MO is the purpose of the two remaining steps. No cycles of this kind have been proposed. Several four and five-steps cycles can be regarded as belonging to this group, e.g. the iron-chlorine process (Knoche and Schubert, 1972; Pangborn and Scharer, 1974):

where the last three reactions are equivalent to:

The first reaction is the key one as it contains only one of the reactants to be chosen:

The change in Gibbs' free energy associated with this step is

$$\Delta G_T = (\Delta G_{\text{MO}}^f - \Delta G_{\text{M}}^f) - \Delta G_{\text{H}_2\text{O}}^f \quad (16)$$

There are no restrictions regarding whether this should be an endothermic or exothermic reaction. We will set limits to the possible values of

ΔG_T :

$$-30 \text{ kcal} \leq \Delta G_T \leq 10 \text{ kcal} \quad (17)$$

considering that if $\Delta G_T > 10$ kcal the equilibrium will be very unfavorable, even at high temperatures. On the contrary, if $\Delta G_T < -30$ kcal the reaction will be very irreversible and the equilibrium for the other two steps very unfavorable. Therefore we must look for pairs M-MO that satisfy the previous inequality, which can be re-written as

$$\left| (\Delta G_{MO}^f - \Delta G_M^f) - \Delta G_{H_2O}^f + 10 \text{ kcal} \right| \leq 20 \text{ kcal} \quad (18)$$

The free energy differences for a large number of M-MO couples were examined from 300 to 1100°K. The nonionic pairs that came within a 20 kcal difference are:

CO-C	Cs ₂ O-Cs	GeO ₂ -Ge	Rb ₂ O-Rb
CO ₂ -C	Fe ₂ O ₃ -Fe	GeO ₂ -GeO	Sb ₂ O ₃ -Sb
CO ₂ -CO	FeO-Fe	In ₂ O ₃ -In	SnO-Sn
CdO-Cd	Fe ₃ O ₄ -Fe	K ₂ O-K	SnO ₂ -SnO
CeO ₂ -Ce ₂ O ₃	Fe ₃ O ₄ -FeO	MoO ₂ -Mo	V ₂ O ₄ -VO
CoO-Co	Ga ₂ O ₃ -Ga	NiO-Ni	WO ₂ -W
Cr ₂ O ₃ -Cr	GeO-Ge	P ₄ O ₁₀ -P	

The reaction $M + H_2O$ does not occur for some of the previous pairs for kinetic reasons. A search was carried out using inorganic chemistry handbooks (Gmelins; Pascal) to identify an X group that would undergo the second and third reactions in the scheme. There is no halogen for which both reactions

take place, not even to a very limited extent.

Type 3 Processes

No process of this kind has been proposed in the literature. A four-step scheme that is similar and can be included here is the Mark I process of De Beni (Euratom, 1973):

In a cycle of this kind the exothermic reaction must be either the first (a) or the third (c). The search is facilitated by using reaction (b), where only M enters. A number of these oxide decompositions that are feasible at temperatures of the order of 1000°C or less are in Table 5. There are two cases: decomposition to a pure metal and decomposition to a lower oxide

and we shall examine them separately.

Mercury is the only non-precious metal corresponding to the first case. Let us consider next reaction (a). Table 6 lists the standard free energy of hydrolysis at different temperatures for a few of the 145 metal halides that we examined. The calculations were based on the solid salt. Of the mercuric halides, the fluoride is the only one that can be hydrolyzed, but the hydrofluoric acid that is obtained will not attack mercury as in reaction (c).

The other case that must be explored is the use of elements with multiple valence states. Table 5 shows several decompositions to lower oxides that could be used as reaction (b). The difficulty in these cases is that the last reaction of the scheme competes with the formation of the lower halide, without production of hydrogen. This fact was pointed out by De Beni (Euratom, 1973). If the couple $\text{CuO}-\text{Cu}_2\text{O}$ is chosen, a conceivable cycle would be:

But what takes place instead of the last reaction is

These competing reactions should be checked for every MO-M couple in the table or even better, their difference. E.g.,

This last reaction should show a negative ΔG_{298}° if hydrogen formation is favored. Table 7 shows the values of ΔG° for a few of these reactions. An extensive search indicates that no three-step process of Type 3 exists.

Type 4 processes

There is no proposed three-step process of this sort, but some multi-step cycles are extensions of it. An example is the Catherine process (Wentorf and Hanneman, 1973):

where the reactions can be added as indicated, to give:

The key step is reaction (b) which requires a decomposable hydride. Thermodynamic information on a few of these decompositions is contained in Table 3. Hydrogen iodide is the only decomposable member of all hydrogen halides at 800°C or less. The Catherine process uses this reaction but in two steps, with nickel iodide as an intermediate. Iodine seems to be the most promising element to be used as X in these kinds of schemes, but a five-step process that uses selenium has also been suggested (Hickman et al., 1974). Its first two steps are:

An undesired reaction takes place here that does not occur for halogens: the formation of the oxide, in this case SeO_2 . Thus selenium, like sulfur, must be rejected for a three-step process.

Iodide volatilization is used as a metal purification technique and therefore much information on iodides has been compiled. In particular with respect to reaction (c) of these schemes (Rolsten, 1961):

"...iodine does not react directly with most oxides, except those of the alkali and alkaline earth metals and perhaps copper and silver, which have a particular affinity for iodine."

and furthermore:

"Iodine does not react with oxygen, nitrogen, hydrogen or carbon compounds of: Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Fe, Bi, Ge, Y, Ni, U, W, Pa, and Si and in general all transition metals."

Type 5 Processes

A few three-step schemes of this kind have been proposed in the literature. The lithium nitrite sequence of Abraham and Schreiner (1973) is:

The others are the sulfur dioxide cycle of Knoche and Schulten:

and the copper-iodine scheme of Schulten:

In these cases M and X can be chosen separately using reactions (b) and (c). Since X does not have to contact oxygen, sulfur and selenium also become possible choices, in addition to iodine. Thermodynamic data for decomposition of their hydrides is shown in Table 3.

There are several oxides that can be decomposed as in reaction (b), and some of them are shown in Table 5. Mercuric oxide is the only one that decomposes to the metal and not to a lower oxide, and therefore the only metal oxide that can be used together with selenium or sulfur.

Reaction (c) is only slightly endothermic (see Table 3). Since the overall ΔH is 68 kcal, reaction (a) is also endothermic. Therefore all of

the reactions are endothermic, which violates the principle mentioned earlier that at least one reaction must be exothermic. Consequently Type 5 processes are not feasible.

Types 6 and 7

Before we consider these processes it is necessary to understand the difference between two and three-step processes. As we have pointed out previously, a Type 1 pattern (see Figure 2) can be considered an extension of the two-step hydride process in which the endothermic decomposition of the hydride has been split into one exothermic and one endothermic step.

Splitting an endothermic reaction into two endothermic steps may simplify the separation of the products but it brings no thermodynamic advantage. Conversely, two endothermic or two exothermic reactions can be combined to a single reaction for the purpose of studying the cycle, without changing the thermodynamic properties.

It is for these reasons that Type 6 pattern is not a true 3-step cycle unless reaction (b) is exothermic. Reaction (c) is obviously endothermic and if reaction (b) were also endothermic, then reactions (b) and (c) can be added to form a 2-step oxide pattern. Since it is known that two-step processes do not work, then reaction (b) must be exothermic.

It is shown in Table 1 that ΔS for the exothermic reaction must be of the order of at least -40 e.u. and perhaps even -80 e.u. Given the

nature of reaction (b), our finding that absolute values of ΔS do not exceed a few entropy units is not surprising. Therefore cycles of Type 6 are impossible.

The same reasoning applied to cycles of Type 7 yields the same negative conclusions.

Conclusion

An initial consideration of the thermodynamic limitations suggests that a minimum of six or seven reaction steps would be necessary so that every reaction in the process can be carried out under not-very-unfavorable conditions. This is essential in order to keep kinetics, separation work and recycles at values compatible with the expected size of hydrogen production operations.

On the other hand, economics impose a severe restriction on the allowable number of reaction steps. The usual case is that each reaction requires at least one other operation (separation, heat exchange, change of phase). Each of these other operations adds to the capital cost and inefficiencies. Thus it becomes difficult to picture a process involving four or more reactions that can successfully compete with direct electrolysis.

These considerations made it essential to verify that a working three-step cycle indeed does not exist. Our broad although not exhaustive search indicated that this probably is the case. The stiff

non-thermodynamic requirements of complete recovery of all reagents and absence of side reactions tend to back this conclusion. Most multi-step processes proposed to date can actually be classified as three-step processes. Therefore there is good reason to doubt the existence of workable thermochemical processes. If one exists, it would contain at least 6 or 7 reactions and probably could not compete with electrolysis.

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Nomenclature

C_p = molar heat capacity at constant pressure, cal/°K mol

ΔG = change in Gibbs' free energy, kcal

ΔH = change in enthalpy, kcal

K = equilibrium constant

P = pressure, atm

Q = heat absorbed, kcal

R = gas constant, kcal/°K mol

T = temperature, °K

W = work, kcal

Subscripts and Superscripts

C = low temperature

H = high temperature

i = i 'th component

y = gas phase mol fraction

o = standard state

I = high temperature step

II = low temperature step

Greek letters

η = energy efficiency

Table No.1. Thermochemical Data for Hypothetical Two-Step Decomposition of Water. In Each Case the First Reaction is Endothermic and the Second is Exothermic.

Process	T °C	ΔG_{298} kcal	ΔH_{298} kcal	ΔS_{298} eu	Equilibrium constant K (at T)	Thermal efficiency η
A	800	56.69	78.50	73.15	1	0.870
	25	0	-10.18	-34.14	1	
B	800	53.96	78.50	82.30	100	0.646
	25	2.73	-10.18	-43.29	0.01	
C	800	59.42	78.50	64.00	0.01	0.387
	25	-2.73	-10.18	-24.99	100	
D	800	59.42	86.05	89.34	100	0.794
	25	-2.73	-17.73	-50.33	100	
E	800	62.15	93.61	105.54	10,000	0.730
	25	-5.46	-25.29	-66.53	10,000	
F	800	77.15	110.61	112.22	100	0.618
	25	-20.46	-42.29	-73.21	10^{15}	

Table No. 2. Thermodynamic Properties for a few Oxide Decompositions.

Reaction	ΔH_{298}° kcal	ΔG_{298}° kcal	ΔS_{298}° eu	min T_H °K
$1/3 \text{ Al}_2\text{O}_3 = 2/3 \text{ Al} + 1/2 \text{ O}_2$	133.2	125.7	24.92	5345
$1/3 \text{ As}_2\text{O}_3 = 2/3 \text{ As} + 1/2 \text{ O}_2$	52.3	45.9	21.57	2426
$\text{As}_2\text{O}_5 = \text{As}_2\text{O}_3 + 1/2 \text{ O}_2$	43.0	35.5	25.16	1709
$\text{BaO} = \text{Ba} + 1/2 \text{ O}_2$	133.5	126.5	23.48	5686
$\text{BeO} = \text{Be} + 1/2 \text{ O}_2$	143.1	136.1	23.48	6095
$\text{BiO} = \text{Bi} + 1/2 \text{ O}_2$	50.0	43.5	21.80	2294
$1/3 \text{ Bi}_2\text{O}_3 = 2/3 \text{ Bi} + 1/2 \text{ O}_2$	46.0	39.5	21.80	2110
$\text{CaO} = \text{Ca} + 1/2 \text{ O}_2$	150.7	143.3	24.82	6070
$\text{CdO} = \text{Cd} + 1/2 \text{ O}_2$	62.2	55.1	23.81	3366
$1/3 \text{ Ce}_2\text{O}_3 = 2/3 \text{ Ce} + 1/2 \text{ O}_2$	145.0	137.2	26.27	5520
$2 \text{ CeO}_2 = \text{Ce}_2\text{O}_3 + 1/2 \text{ O}_2$	55.0	48.5	21.80	2523
$\text{CoO} = \text{Co} + 1/2 \text{ O}_2$	57.0	51.6	18.11	$>10^4$
$1/3 \text{ Cr}_2\text{O}_3 = 2/3 \text{ Cr} + 1/2 \text{ O}_2$	90.9	84.4	21.79	4171
$\text{Cs}_2\text{O} = 2 \text{ Cs} + 1/2 \text{ O}_2$	76.0	65.0	36.89	2060
$\text{Cu}_2\text{O} = 2 \text{ Cu} + 1/2 \text{ O}_2$	40.4	35.0	18.11	2231
$\text{CuO} = \text{Cu} + 1/2 \text{ O}_2$	37.6	31.0	22.13	1699

Table No. 3. Comparison of Hydride Decompositions with Water Decomposition.

Reaction	ΔH_{298}° kcal	ΔG_{298}° kcal	ΔS_{298}° eu
$\text{H}_2\text{O(g)} = \text{H}_2 + 1/2 \text{ O}_2$	57.80	54.64	10.60
$2 \text{ HCl} = \text{H}_2 + \text{Cl}_2$	44.12	45.56	-4.83
$2 \text{ HF} = \text{H}_2 + \text{F}_2$	128.40	129.40	-3.35
$2 \text{ HBr} = \text{Br}_2(\text{l}) + \text{H}_2$	17.32	25.44	-27.23
$2 \text{ HI} = \text{I}_2(\text{s}) + \text{H}_2$	-12.40	-0.62	-39.50
$2 \text{ HI} = \text{I}_2(\text{g}) + \text{H}_2$	2.48	4.04	-5.13
$\text{H}_2\text{S} = \text{S(c)} + \text{H}_2$	4.82	7.89	-10.30
$\text{H}_2\text{S} = 1/8 \text{ S}_8(\text{g}) + \text{H}_2$	7.85	9.36	-5.06
$\text{H}_2\text{Se} = \text{Se(c)} + \text{H}_2$	-20.50	-17.00	-11.74

Table No. 4. Thermodynamic Properties for the Dissociation of Selected Chlorides.

Reaction	ΔG_{298}^C kcal	$\Delta G_{298}^C / \Delta S_{298}^C$ °K
$2 \text{ AgCl}(c) = 2 \text{ Ag}(c) + \text{Cl}_2$	52.44	1888
$2/3 \text{ BiCl}_3(g) = 2/3 \text{ Bi}(l) + \text{Cl}_2$	53.19	2195
$\text{CdCl}_2(c) = \text{Cd}(c) + \text{Cl}_2$	81.90	2195
$\text{CoCl}_2(c) = \text{Co}(c) + \text{Cl}_2$	67.50	1953
$2/3 \text{ CrCl}_3(c) = 2/3 \text{ Cr}(c) + \text{Cl}_2$	78.66	2119
$2 \text{ CrCl}_3(c) = 2 \text{ CrCl}_2(c) + \text{Cl}_2$	67.50	1362
$2 \text{ CuCl}(c) = 2 \text{ Cu}(c) + \text{Cl}_2$	57.80	2100
$\text{HgCl}_2(g) = \text{Hg}(g) + \text{Cl}_2$	47.27	1714
$\text{NiCl}_2(c) = \text{Ni}(c) + \text{Cl}_2$	61.90	1663
$\text{PbCl}_2(c) = \text{Pb}(l) + \text{Cl}_2$	75.91	2000
$\text{PdCl}_2(c) = \text{Pd}(c) + \text{Cl}_2$	42.26	1281
$\text{UCl}_5(c) = \text{UCl}_3(c) + \text{Cl}_2$	40.5	1404
$2 \text{ VCl}_3(c) = 2 \text{ VCl}_2(c) + \text{Cl}_2$	35.00	1159
$\text{ZnCl}_2(c) = \text{Zn}(c) + \text{Cl}_2$	88.26	2362

Table No. 5. Thermodynamic Properties of Easily Decomposable Oxides.

Reaction	ΔG_{298}° kcal	ΔS_{298}° eu	$\Delta G^{\circ}/\Delta S^{\circ}$ °K
$1/2 \text{As}_2\text{O}_5(\text{c}) = 1/2 \text{As}_2\text{O}_3(\text{c}) + 1/2 \text{O}_2$	23.4	24.65	949
$2 \text{CuO} = \text{Cu}_2\text{O} + 1/2 \text{O}_2$	27.0	26.16	1032
$\text{Hg}_2\text{O} = 2 \text{Hg}(\text{l}) + 1/2 \text{O}_2$	13.0	30.19	430
$\text{HgO} = \text{Hg}(\text{l}) + 1/2 \text{O}_2$	13.9	25.93	539
$3 \text{Mn}_2\text{O}_3 = 2 \text{Mn}_3\text{O}_4 + 1/2 \text{O}_2$	19.9	16.43	1211
$2 \text{MnO}_2 = \text{Mn}_2\text{O}_3 + 1/2 \text{O}_2$	12.1	25.49	475
$3/2 \text{MnO}_2 = 1/2 \text{Mn}_3\text{O}_4 + 1/2 \text{O}_2$	14.1	23.24	605
$\text{Pb}_3\text{O}_4 = 3 \text{PbO} + 1/2 \text{O}_2$	12.4	23.48	526
$3/2 \text{PbO}_2 = 1/2 \text{Pb}_3\text{O}_4 + 1/2 \text{O}_2$	4.7	22.47	209
$\text{PbO}_2 = \text{PbO} + 1/2 \text{O}_2$	7.1	22.14	318
$\text{Rb}_2\text{O}_2 = \text{Rb}_2\text{O} + 1/2 \text{O}_2$	17.0	18.45	921
$\text{Rb}_2\text{O}_3 = \text{Rb}_2\text{O}_2 + 1/2 \text{O}_2$	9.0	20.12	447
$1/2 \text{Rb}_2\text{O}_3 = 1/2 \text{Rb}_2\text{O} + 1/2 \text{O}_2$	13.0	19.29	674
$\text{SrO}_2 = \text{SrO} + 1/2 \text{O}_2$	7.0	18.11	387
$1/2 \text{Tl}_2\text{O}_3 = 1/2 \text{Tl}_2\text{O} + 1/2 \text{O}_2$	19.7	24.99	788

Table No. 6. Free Energy of Hydrolysis for a few Halides, in kcal.

Reaction	Temperature, °K				
	300	500	700	900	1100
$\text{H}_2\text{O} + 2/3 \text{AlF}_3 = 1/3 \text{Al}_2\text{O}_3 + 2 \text{HF}$	5.66	-1.73	-6.58	-11.60	-16.38
$\text{H}_2\text{O} + 2/3 \text{AlCl}_3 = 1/3 \text{Al}_2\text{O}_3 + 2 \text{HCl}$	-12.63	-18.58	-22.06		
$\text{H}_2\text{O} + 2/3 \text{AlBr}_3 = 1/3 \text{Al}_2\text{O}_3 + 2 \text{HBr}$	-12.55	-15.58	-22.06		
$\text{H}_2\text{O} + 2/3 \text{AlI}_3 = 1/3 \text{Al}_2\text{O}_3 + 2 \text{HI}$	-16.77	-23.05	-26.86		
$\text{H}_2\text{O} + 2 \text{AgF} = \text{Ag}_2\text{O} + 2 \text{HF}$	13.79	6.30	0.69		
$\text{H}_2\text{O} + 2 \text{AgCl} = \text{Ag}_2\text{O} + 2 \text{HCl}$	60.89	53.62	48.77		
$\text{H}_2\text{O} + 2 \text{AgBr} = \text{Ag}_2\text{O} + 2 \text{HBr}$	74.35	67.12	62.49		
$\text{H}_2\text{O} + 2 \text{AgI} = \text{Ag}_2\text{O} + 2 \text{HI}$	86.41	79.22	74.59		
$\text{H}_2\text{O} + \text{BaF}_2 = \text{BaO} + 2 \text{HF}$	74.58	66.45	60.74	54.42	49.07
$\text{H}_2\text{O} + \text{BaCl}_2 = \text{BaO} + 2 \text{HCl}$	77.81	69.97	63.38	56.18	49.97
$\text{H}_2\text{O} + \text{BaBr}_2 = \text{BaO} + 2 \text{HBr}$	79.68	71.42	64.75	57.49	51.16
$\text{H}_2\text{O} + \text{BaI}_2 = \text{BaO} + 2 \text{HI}$	73.77	65.57	59.56	52.96	47.29
$\text{H}_2\text{O} + \text{HgF}_2 = \text{HgO} + 2 \text{HF}$	-3.70	-12.05	-17.69		
$\text{H}_2\text{O} + \text{HgCl}_2 = \text{HgO} + 2 \text{HCl}$	39.38	32.02	28.26		
$\text{H}_2\text{O} + \text{HgBr}_2 = \text{HgO} + 2 \text{HBr}$	52.94	45.32	41.34		
$\text{H}_2\text{O} + \text{HgI}_2 = \text{HgO} + 2 \text{HI}$	66.80	59.07	55.29		

Table No. 7.

Reaction	ΔG_{298}° kcal	ΔS_{298}° eu
$\text{Cu}_2\text{F}_2 + 2 \text{ HF} = 2 \text{ CuF}_2 + \text{H}_2$	4.73	-33.98
$\text{CoF}_2 + 2 \text{ HF} = 2 \text{ CoF}_3 + \text{H}_2$	76.7	-14.5
$2 \text{ MnF}_2 + 2 \text{ HF} = 2 \text{ MnF}_3 + \text{H}_2$	44.7	-41.4
$2 \text{ MnCl}_2 + 2 \text{ HCl} = 2 \text{ MnCl}_3 + \text{H}_2$	58.4	-37.03
$\text{PbF}_2 + 2 \text{ HF} = \text{PbF}_4 + \text{H}_2$	75.5	-36.5
$\text{SbCl}_3 + 2 \text{ HCl} = \text{SbCl}_5 + \text{H}_2$	37.85	-24.13

FIGURES

1. Two-Step Standard Patterns.
2. Three-Step Standard Patterns.

Oxide Processes

Hydride Processes

Figure No 1.

Type 1

Type 3

Type 5

Type 6

Type 2

Type 4

Type 7

Figure No 2.

TABLE 2

Some Easily Decomposable Oxides

Reaction	ΔG° Kcal	ΔH° Kcal	ΔS° eu
$\text{Ag}_2\text{O} = 2\text{Ag} + 1/2 \text{O}_2$	2.68	7.42	15.91
$1/2 \text{As}_2\text{O}_5 = 1/2 \text{As}_2\text{O}_3 + 1/2 \text{O}_2$	23.4	--	24.65
$2\text{CrO}_2 = \text{Cr}_2\text{O}_3 + 1/2 \text{O}_2$	6.86	12.35	18.42
$\text{Co}_3\text{O}_4 = 3 \text{CoO} + 1/2 \text{O}_2$	27.2	36.0	29.53
$2\text{CuO} = \text{Cu}_2\text{O} + 1/2 \text{O}_2$	27.00	34.80	26.17
$\text{Hg}_2\text{O} = 2\text{Hg}(\ell) + 1/2 \text{O}_2$	13.00	21.80	29.53
$\text{HgO} = \text{HgO}(\ell) + 1/2 \text{O}_2$	14.00	21.68	25.77
$2\text{MnO}_2 = \text{Mn}_2\text{O}_3 + 1/2 \text{O}_2$	12.10	19.70	25.50
$3/2 \text{MnO}_2 = 1/2 \text{Mn}_3\text{O}_4 + 1/2 \text{O}_2$	14.05	20.98	23.26
$\text{Pb}_3\text{O}_4 = 3\text{PbO} + 1/2 \text{O}_2$	11.75	18.15	21.48
$3/2 \text{PbO}_2 = 1/2 \text{Pb}_3\text{O}_4 + 1/2 \text{O}_2$	4.70	11.40	22.48
$\text{PbO}_2 = \text{PbO} + 1/2 \text{O}_2$	7.05	13.65	22.15
$\text{Rb}_2\text{O}_2 = \text{Rb}_2\text{O} + 1/2 \text{O}_2$	17.00	--	18.45
$\text{Rb}_2\text{O}_3 = \text{Rb}_2\text{O}_2 + 1/2 \text{O}_2$	9.00	--	20.45

TABLE 3

Possible Candidates for
Electrochemical Oxide Decomposition

Reaction	ΔG° Kcal	ΔH° Kcal
$1/5 \text{ As}_2\text{O}_5 = 2/5 \text{ As} + 1/2 \text{ O}_2$	36.9	43.7
$\text{As}_2\text{O}_5 = \text{As}_2\text{O}_4 + 1/2 \text{ O}_2$	35.5	43.0
$\text{CO} = \text{C} + 1/2 \text{ O}_2$	32.8	26.4
$\text{CuO} = \text{Cu} + 1/2 \text{ O}_2$	30.85	37.50
$\text{Cu}_2\text{O} = 2\text{Cu} + 1/2 \text{ O}_2$	35.4	40.8
$1/4 \text{ Pb}_3\text{O}_4 = 3/4 \text{ Pb} + 1/2 \text{ O}_2$	36.88	43.88
$1/3 \text{ RbO}_3 = 2/3 \text{ Rb} + 1/2 \text{ O}_2$	31.80	50.75
$1/2 \text{ TeO}_2 = 1/2 \text{ Te} + 1/2 \text{ O}_2$	37.3	38.85
$1/2 \text{ TlO}_2 = 1/2 \text{ Tl} + 1/2 \text{ O}_2$	36.6	43.2
$\text{Bi}_2\text{O}_3 = 2\text{BiO} + 1/2 \text{ O}_2$	31.50	38.00
$1/2 \text{ RbO}_2 = 1/2 \text{ Rb} + 1/2 \text{ O}_2$	26.25	31.50
$1/3 \text{ TcO}_3 = 1/3 \text{ Tc} + 1/2 \text{ O}_2$	36.67	43.0

TABLE 4

Possible Candidates for
Electrochemical Chloride Decomposition

Reaction	ΔG° Kcal	ΔH° Kcal
$2\text{CuCl}_2 = 2\text{CuCl} + \text{Cl}_2$	26.7	39.6
$2\text{MgCl} = 2\text{Mg} + \text{Cl}_2$	32.0	20.0
$2/3 \text{ReCl}_3 = 2/3 \text{Re} + \text{Cl}_2$	30.0	42.0
$2/5 \text{SbCl}_5 = 2/5 \text{Sb} + \text{Cl}_2$	31.96	37.7
$2\text{TiCl}_4 = 2\text{TiCl}_2 + \text{Cl}_2$	35.01	19.8
$2/3 \text{TlCl}_3 = 2/3 \text{Tl} + \text{Cl}_2$	28.53	48.6

TABLE 5

Possible Candidates for
Electrochemical Hydrolysis Reactions

Reaction	ΔG° Kcal	ΔH° Kcal
$H_2O + 2Ag = 2AgOH + H_2$	32.52	38.58
$H_2O + 1/2 As_2O_3 = 1/2 As_2O_5 + H_2$	32.44	35.52
$H_2O + 3CoO = Co_3O_4 + H_2$	29.49	32.32
$H_2O + Cu_2O = 2CuO + H_2$	29.69	33.52
$H_2O + MnO = MnO_2 + H_2$	32.09	35.92
$H_2O + 2 Mn_3O_4 = 3Mn_2O_3 + H_2$	36.79	43.52
$H_2O + 1/2 Pb = 1/2 PbO_2 + H_2$	30.54	35.27
$H_2O + 3/2 Pr_2O_3 = 1/2 Pr_6O_{11} + H_2$	36.44	41.32
$H_2O + 1/2 Rb = 1/2 RbO_2 + H_2$	30.44	36.82
$H_2O + 1/2 Ru = 1/2 RuO_2 + H_2$	34.69	40.07
$H_2O + 1/2 Se = 1/2 SeO_2 + H_2$	35.94	40.82
$H_2O + Si = SiO + H_2$	28.49	46.59
$H_2O + 2/3 Tl = 1/3 Tl_2O_3 + H_2$	31.36	35.82
$H_2O + 1/2 Tl = 1/4 Tl_2O_4 + H_2$	35.07	39.90
$H_2O + V_2O_4 = V_2O_5 + H_2$	31.19	37.32

TABLE 6

Hydrogen Producing Reactions

Reaction	ΔG° Kcal	ΔH° Kcal
$H_2O + 2/3 Al = 1/3 Al_2O_3 + H_2$	-69.07	-64.88
$2H_2O + Ba = Ba(OH)_2 + H_2$	-95.82	-101.94
$H_2O + Ca = CaO + H_2$	-86.53	-82.33
$H_2O + 1/2 CaH = 1/2 Ca(OH)_2 + H_2$	-33.06	-27.27
$H_2O + C = CO + H_2$	23.88	41.90
$H_2O + 3/2 Fe = 1/2 Fe_3O_4 + H_2$	-66.72	-65.33
$H_2O + Fe + CO_2 = FeCO_3 + H_2$	-10.46	-25.15
$2H_2O + 2Na = 2NaOH + H_2$	-86.99	-87.84
$2H_2O + SO_2 = H_2SO_4 + H_2$	7.83	-9.3
$H_2O + Zn = ZnO + H_2$	-19.41	-14.93

TABLE 7

Possible Candidates for
Electrochemical Iodine Reactions

Reaction	ΔG° Kcal	ΔH° Kcal
$1/3 \text{ As}_2\text{O}_3 + \text{I}_2 = 2/3 \text{ AsI}_3 + 1/2 \text{ O}_2$	35.33	41.83
$1/2 \text{ Ce}_2\text{O}_3 + \text{I}_2 = 2/3 \text{ CeI}_3 + 1/2 \text{ O}_2$	29.83	36.33
$\text{CoO} + \text{I}_2 = \text{CoI}_2 + 1/2 \text{ O}_2$	29.8	36.3
$\text{MnO} + \text{I}_2 = \text{MnI}_2 + 1/2 \text{ O}_2$	29.25	34.95
$1/3 \text{ Nd}_2\text{O}_3 + \text{I}_2 = 2/3 \text{ NdI}_3 + 1/2 \text{ O}_2$	33.50	38.72
$\text{NiO} + \text{I}_2 = \text{NiI}_2 + 1/2 \text{ O}_2$	27.6	34.2
$1/3 \text{ Pr}_2\text{O}_3 + \text{I}_2 = 2/3 \text{ PrI}_3 + 1/2 \text{ O}_2$	33.50	37.67
$1/3 \text{ Sb}_2\text{O}_3 + \text{I}_2 = 2/3 \text{ SbI}_3 + 1/2 \text{ O}_2$	33.63	40.97

TABLE 8

Some Hydride Decompositions

Reaction	ΔG° Kcal	ΔH° Kcal
$H_2O(l) = H_2(g) + 1/2 O_2(g)$	56.69	68.32
$HF(g) = 1/2 H_2(g) + 1/2 F_2(g)$	65.30	64.80
$HF(aq) = 1/2 H_2(g) + 1/2 F_2(g)$	70.95	76.50
$HCl(g) = 1/2 H_2(g) + 1/2 Cl_2(g)$	22.78	22.06
$HCl(aq) = 1/2 H_2(g) + 1/2 Cl_2(g)$	31.37	39.95
$HBr(g) = 1/2 H_2(g) + 1/2 Br_2(g)$	12.77	8.70
$HBr(aq) = 1/2 H_2(g) + 1/2 Br_2(g)$	24.85	29.05
$HI(g) = 1/2 H_2(g) + 1/2 I_2(g)$	-0.41	-6.33
$HI(aq) = 1/2 H_2(g) + 1/2 I_2(g)$	12.33	13.19
$H_2S(g) = H_2(g) + S(g)$	8.02	4.93
$H_2S(aq) = H_2(g) + S(s)$	6.66	9.50
$H_2Se(g) = H_2(g) + Se(s)$	-3.8	-7.1
$H_2Se(aq) = H_2(g) + Se(s)$	-5.3	-4.6