Hydrogen and Energy

by C. Marchetti

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1. Introduction

The challenge of the century for chemical engineers—thermochemical cycles to produce hydrogen—may bring a revolution in the technology and management of energy and food.

Hydrogen has a peculiar position in nature:
—it is the most abundant element;
—it plays a key role in fueling the universe;
—it is the first chemical product in photosynthesis i.e. the chemical mediator between sunlight and the biosphere.

Hydrogen can become the main energy mediator between the newly harnessed nuclear energy and human society, so avoiding most of the political, ecological, long-term procurement problems connected with the use of fossil fuels. Via proper microorganisms it can be employed to produce "primary" food, easing the pressure on agriculture. This fact will have even more revolutionary consequences.

2. The Objective

Practically all the energy we use comes from the sun. Directly via the biosphere and fairly indirectly via the fossil fuels, which can be considered long-term stores of solar energy. Nuclear energy provides a completely independent energy source, much larger energy reserves and a very different geopolitical distribution of the raw materials: uranium and thorium. And so it is natural to try to link our energy system to this new source.

Up to now, however most of the research and development effort has been concentrated on the production of electricity, and for good reason. In fact, a substantial 20-25% of the primary energy input in a developed society is used to make electricity whose production is concentrated in large units where reactors can better show their economics. But almost nothing has been done to penetrate the remaining three quarters of the primary energy market that is, fuel, ore processing and miscellaneous, where our society is geared to burning a wide variety of chemicals.

The fact is that nuclear reactors are essentially very large sources of heat, that the energy market is split in a host of small customers; and that heat is not easily transportable and storable. So, in analogy with the electric system, the problem was set to find a flexible intermediate, producible in large blocks, into which nuclear heat can be stored as chemical energy and economically distributed.

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The reflections and discussions that went on in various places in the world, from the late sixties, have brought the consensus of the scientific and technological community, to point at hydrogen as the candidate global energy carrier. Hydrogen in fact has a certain number of very desirable properties:

(1) It can be produced from water, a cheap and plentiful raw material.
(2) When burned, it reverts to water, a nonpolluting chemical.
(3) It can be transported overland by pipeline at low cost, and by sea, in tankers, as liquid hydrogen.
(4) It can be easily stored, particularly in ground structures, like exhausted gas fields.
(5) It has an extreme flexibility of utilization with great advantages in many cases over current fuels e.g. for airplanes, and for fuels cells. Practically all the energy market can be covered by hydrogen.
(6) Following points 3, 4, 5, it can be produced in very large units e.g. of 1000 gigawatt order, so that it can best use the economy of size, whenever technologically possible.
(7) It has already a large market as a chemical, a very important strategic asset as it will be seen.

The most important, or at least the most publicized, drawback is that it is quite inflammable anl explosive. But a deeper scrutiny on this point shows that, all considered, it is not really worse than natural gas, a fuel fully accepted in industry and in the homes.

Given the atom as the primary energy source and hydrogen as the ideal energy carrier, the objective of our research was stated since the beginning very simply: find the best process to produce hydrogen from water using heat of the grade available from commercial ,nuclear reactors.

3. The Means

The discussion of the means to produce hydrogen leads us to the core of the problem: heat being available at temperatures of 300°C (water-cooled nuclear reactors) or at 500°-800°C (high temperature gas reactor), how can we use it to break the water molecule and produce hydrogen and oxygen?

An apparently straightforward solution would be that of making electricity and electrolyzing water. Unhappily it is a very twisted one, because this poor energy is handled many times, to make steam first in the boiler, then mechanical energy in the turbine, then in the generator electrical energy, which is rectified, and fed to the electrolyzer.

All that piles up capital and cascades inefficiencies.

It is true that industrial electrolyzers, looked at as electrical machines, are very inefficient (50% of the theoretical), very "diluted" (less than a Watt/cm²), and very expensive ($150/kW) so one might conceivably think these electrolyzers could find someday their Edison or their Newton to improve dramatically their efficiency. But even with unit efficiency and zero capital cost, their potential for producing what, after all, is just a fuel, from a sophisticated form of energy like electricity did appear to us very dim.

Now the simplest way to break a molecule is to heat it until it cracks, a well-known and much used process. But water molecules are very tough indeed and start breaking in sizable fractions around 2,500°C, a temperature well above the potential of present-day commercial reactors.

Following the old proverb: "If you can't carry a load in one journey, make two", we thought of breaking the water molecule in two steps or more if necessary, with the help of intermediate chemical products, each step requiring heat at temperatures available in commercial reactors.

The second condition, to make the process a clean transformation of just molecular heat into chemical energy, was that all the chemicals involved should be recycled. Respecting these conditions our process could be visualized as a black box containing chemicals, where the inputs are heat and water, and the outputs oxygen and hydrogen, plus some "degraded" heat.

The background philosophy in looking for a chemical process as a competitor to electrolysis was based on these points:

—Thermochemical processes tend to be much cheaper than electrochemical ones, per unit of energy handled.
—The energy would hopefully be handled only once, while in electrolysis it is handled four of five times.
—Processes to make electricity (and electrolysis) rely on mature technology and important breakthroughs appear improbable.
—The history of new chemical processes, e.g. in petrochemistry and plastics, shows very steep learning curves.
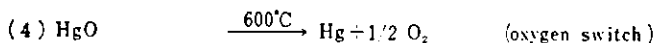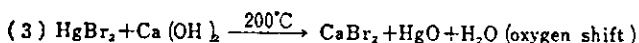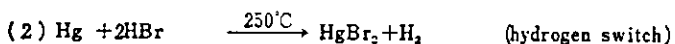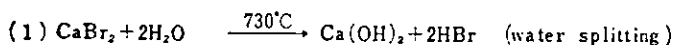Starting from the considerations and respecting the conditions imposed, M. De Beni invented our first process, Mark-1, using Ca, Br, and Hg compounds as the recyclable chemicals[1].

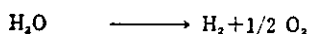(1) Thermochemical Processes for Water Splitting

The Mark-1 cycle

This four-step chemical cycle was found by De Beni in 1969 (Fig. 3) and it is briefly described in[2]. It works with compounds of mercury, bromine and calcium.

The following is a set of reactions in the cycle:

(1) $CaBr_2 + 2H_2O \xrightarrow{730°C} Ca(OH)_2 + 2HBr$ (water splitting)

(2) $Hg + 2HBr \xrightarrow{250°C} HgBr_2 + H_2$ (hydrogen switch)

(3) $HgBr_2 + Ca(OH)_2 \xrightarrow{200°C} CaBr_2 + HgO + H_2O$ (oxygen shift)

(4) $HgO \xrightarrow{600°C} Hg + 1/2\ O_2$ (oxygen switch)

Whose sum is:

$H_2O \longrightarrow H_2 + 1/2\ O_2$

The attractive characteristics of the Mark-1 process are the following:

(a) The maximum temperature required is 730°C, that means about 850°C for the primary nuclear reactor coolant, a temperature well in the range of actual HTGR's; it can however profit from higher temperatures when the development of the HTGR's makes them available.
(b) The system has a single purpose. i.e. all the heat from the reactor is efficiently used to produce hydrogen.
(c) All reaction products are easily separated.
(d) All by-products formed during the reactions can be reinjected at some points in the cycle, permitting a virtual 100% recovery of the chemicals without sideloops.

The principal drawbacks of the process are:

(a) The use of mercury with the related problems of potentially high inventory costs and the possibility of pollution in case of leakage has been much criticized. For this reason we have dedicated much effort to the kinetics of reaction 2 where most of the mercury in the metal state is held.
As shown in Fig. 7 we can now run this reaction at a very high rate, so that the inventory may be less than one m³ Hg/Gwth of input in the plant.
Also from the point of view of availability of Hg we feel pretty safe. Our computer[58] indicates the existence of Hg minerals capable of yielding some million tons of Hg at prices substantially equal to the present ones.
(b) The use of highly corrosive chemicals, especially hydrobromic acid, and the consequent problems in relation to construction materials.
(c) The large amount of materials circulation per unit product.

Chemical studies[3]

Very little information on the reactions involved in the Mark-1 cycle was found in the literature and so we undertook an experimental program aimed at determining their equilibria and kinetics.

(1) On the hydrolysis reaction we found a paper by Robinson et al.[4] which describes a series of experiments where various salts, such as halides, sulfates, phosphates and carbonates of alkaline earths, were hydrolized. The experimental tests were performed in a way that they did not allow the determination of equilibrium values for the hydrolysis, however, they did show that, in the halide family, the most hydrolyzable salt is calcium bromide.

Our experiments on the hydrolysis of calcium bromide were done first using steam at 1 atm; in this condition we can expect the formation of calcium hydroxide up to the temperature of 500°C and the formation of calcium oxide at higher temperatures. Using the data of Brewer[5] and the Bulletin of the Bureau of Mines[6] the computed values for the equilibrium constant range from 8.10^{-10} at 227°C to $3.5\ 10^{-6}$ at 727°C. From our tests we found that values for the equilibrium constant did range from $2.9\ 10^{-7}$ at 300°C to $1.12\ 10^{-2}$ at 727°C. Our calculated and experimental values are presented in Fig. 4.

Other tests with 20 atm. steam led to an apparent equilibrium constant of $1.9\ 10^{-2}$ at 727°C while additional tests with 37 atm. steam yielded an equilibrium constant of 5.10^{-2} at 800°C:

The minimum working pressure necessary to produce $Ca(OH)_2$ has been determined by measuring the decomposition pressure of calcium hydroxide at temperatures

up to 800°C (Fig. 5). The advantage of going to $Ca(OH)_2$ is that the endothermicity of the reaction is much reduced.

The rate and equilibria of hydrolysis have a very strong feedback on the efficiency and economy of the process, so we are investigating this reaction in detail. For example, experimental work is in progress to evaluate a flow sheet based on a temperature of 830°C for the hydrolysis reaction producing HBr at concentrations as high as 60% by wt. The boiling point of $CaBr_2$ being 820°C in this temperature range, the hydrolysis reaction may occur partially or totally in the gas phase. According to these conditions, studies are in progress for evaluating this possibility.

The advantages come from an amelioration of the thermal efficiency; the HBr concentration step being suppressed; and from a strong increase in the reaction rate of mercury with HBr, with the consequent decrease of the inventory of this element in the process (see later). These variants are developed to be prepared to take advantage of a possible increase in temperature of the HTGR's.

(2) Also on the reaction between mercury and hydrobromic acid, there was no valuable information in the literature and we had to start from scratch, i.e. trying to see if the reaction occurs at all.

The experiments were originally made by reacting a mercury drop in glass vials with an excess of concentrated hydrobromic acid 48% by wt. The temperature dependence of rate constant is shown in Fig. 6. Fig. 7 shows the very strong influence of hydrobromic acid concentration on the rate of hydrogen formation at 200°C.

Analytical problems that did arise in the determination of the reaction products have been solved and the analytical procedure is described by Serrini[6]. Due to the overpotential for hydrogen evolution over mercury surface we also tested the effectiveness of some metals as depolarizers.

Some observations during this research led us to foresee the possibility of reacting mercury and hydrobromic acid at temperatures below 200°C. The purpose was to use for this endothermic reaction low grade heat recuperation from other steps of the process in order to improve the total efficiency.

A different way to react mercury with HBr was in fact found by Schütz[14], our mercury specialist, using the intermediate reaction:

$$Hg_2Br_2 + 2HBr \xrightleftharpoons{\hspace{1cm}} 2HgBr_2 + H_2$$
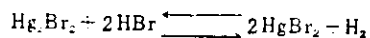
The rate of this reaction is already quite high in the temperature range between 90°C and 125°C. It requires precise control because it is strongly dependent on the ratio of hydrobromic acid and mercurous bromide. The mercurous bromide can be prepared by reacting mercury with a solution of mercuric bromide (in hydrobromic acid) according to the equation:

$$HgBr_2 + Hg \longrightarrow Hg_2Br_2$$
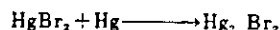
(3) About the reaction of mercury bromide with calcium hydroxide no information at all was available in the literature. The first tests did show that a brown precipitate is obtained. After boiling the solution for some minutes this brown precipitate is transformed into the usual red mercuric oxide. Nevertheless, a certain amount of mercuric bromide is held in solution by the calcium bromide formed. For this reason we have

studied the influence of temperature, initial concentration of mercuric bromide, and the excess of calcium hydroxide.

(4) The dissociation of mercuric oxide is the only step of the Mark-1 cycle for which data were available in the literature. Dissociation pressure have been measured[9] and are known with a sufficient accuracy for our needs. In Fig. 8, HgO dissociation pressure versus temperature is shown. Between 450°C and 600°C the dissociation pressure varies from 1 to 20 atm.; this range is well suitable for practical applications.

Since we need to know also the rate of recombination of oxygen and mercury vapor in order to define how fast the vapors must be cooled to avoid excessive back-reaction, we are also studying the kinetics of HgO formation for temperatures up to 650°C and pressures up to 30 atm.

Many other chemical and physicochemical data are measured or collected, e.g. the vapor pressure of concentrated calcium bromide solutions; the heat of dehydratation of calcium bromide: the pressures and phase composition for the liquid-vapor equilibrium in the ternary system H_2O-HBr-$HgBr_2$.

The flowsheet

A block diagram of the cycle is shown in Fig. 1. The basic flowsheet is given in Fig. 9, reference temperatures are also given. (HF represents the circulation of the heating fluid).

In order to reduce to a minimum and hopefully suppress the stripper and concentrator the hydrolysis reaction of $CaBr_2$ is realized in two steps: 60% at 750°C and the rest at 780°C. It has been experimentally verified that in this way the hydrobromic acid is produced at the azeotropic concentration, 48% by wt.

The maximum temperature in the cycle is always compatible with the 50°C originally foreseen as the maximum temperature available for the primary nuclear reactor coolant.

The thermal efficiency

The efficiency can be defined as the ratio between H_2 combustion heat and the primary heat necessary to produce it. Such definition is somehow equivocal because the higher and lower combustion heats are quite different for hydrogen. Including the heat of condensation of water one has 3,000kcal/Nm³, excluding it 2,500kcal/Nm³.

Thermodynamically it is more convenient to use the higher combustion heat, but when one burns hydrogen in air usually water is not condensed and the lower combustion heat should be considered. Unless otherwise stated we use the lower value. With the heat source at 750°C, the heat sink at 25°C, and operating the water decomposition process in a reversible way, with materials (water, hydrogen and oxygen) entering and leaving the process at 25°C and 1 atm. (i.e. using the higher combustion heat) the thermodynamical efficiency is 85%[13] [15].

To calculate our practical efficiencies we made a computerized model of the plant. The model however is used mainly to assess the sensitivity of the flow sheet toward the different physical parameters, in order to evaluate and balance our research efforts. The calculated efficiencies keep changing and tend to increase with time. Our latest figures give 55% (using the lower heating value of the hydrogen produced).

The structural materials

The chemicals circulating in the various steps of the process are hydrobromic acid (vapor and solution), mercury (salts and vapor); calcium bromide and calcium hydroxide as solids or in solution; oxygen, hydrogen and water. For most of them fairly compatible materials are available for most of the range of temperatures in which we are interested.

Problems arise with hydrobromic acid. About this product little is known, and indication of its ability to attack materials derived from the behavior of hydrochloric acid.

We are screening metallic materials and refractories glazes. The most resistant in the critical range of 200°-600°C are Tantalum, Molybdenum, Zirconium-Niobium alloys, Zircaloy-2, Niobium, Alumina. We are also testing stainless steels.

The short-term objective is to select the materials for a pilot plant. The materials for a large plant are beyond our present scope since they require a very large screening and development effort, as it is always the case with new chemical processes.

Mark-1 family

The lines of development of Mark-1 take into consideration the possibility of substituting some of the elements which are employed. In particular we may use:

Cu instead of Hg: The essential advantage may be the elimination of Hg, the disadvantage is that a higher maximum temperature is required (about 900°C) for the decomposition of copper oxide. The reaction foreseen is not the complete dissociation of CuO, formed in the reaction between $CuBr_2$ and $Ca(OH)_2$ but the partial decomposition of CuO to Cu_2O and O_2; the Cu_2O must then be reacted with the hydrobromic acid.

Sr instead of Ca: The advantage could be essentially a simplification of the flow sheet. It is more difficult however to hydrolize $SrBr_2$ than $CaBr_2$, but we may have reactions 3 and 4 of Mark-1 carried through in just one step. The SrO, which is formed in the hydrolysis, could then react with $HgBr_2$ yielding $SrBr_2$ and the reaction could occur in such a way that mercury and oxygen are formed separately and not as an oxide.
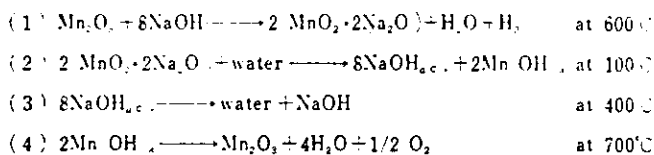
Mark-2

Manganese cycles

This case is representative of the various cycles potentially interesting on thermodynamical grounds, but still "hooked" somewhere. We keep applying to them some laboratory work and much reflection in order to see if they can be disentangled. This philosophy has been very successful with Mark-1 and we have reasons to think it will be also successful with this cycle.
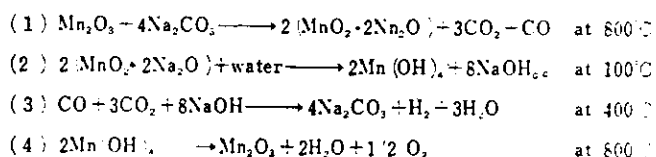
Alkali hydroxides are able to react with some metals to give mixed oxides and hydrogen. In an article by Williams and al.[11] it has been claimed that sodium hydroxide reacts with manganese at temperatures higher than 600°C oxidizing it to MnO_2, and liberating hydorgen.

If between is the oxides of manganese MnO_2 in the stable form in molten sodium hydroxide, then the following cycle becomes possible:

(1) $Mn_2O_3 + 8NaOH \longrightarrow 2 (MnO_2 \cdot 2Na_2O) + H_2O + H_2$ at 600°C

(2) $2 MnO_2 \cdot 2Na_2O + water \longrightarrow 8NaOH_{ac} + 2Mn(OH)_4$ at 100°C

(3) $8NaOH_{ac} \longrightarrow water + NaOH$ at 400°C

(4) $2Mn(OH)_4 \longrightarrow Mn_2O_3 + 4H_2O + 1/2 O_2$ at 700°C

Thermodynamic data for the $MnO_2 (Na_2O)_2$ compound is lacking, so we decided to do some tests to check the reaction between Mn_2O_3 and NaOH. In spite of the results given by Williams we did not observe any reaction; even the substitution of KOH for NaOH did not give more positive results. In fact, when reacting manganese metal with the alkali hydroxide, the maximum valence state we obtained so far is 3.

We have tried to modify the chemical cycle by using alkali carbonates in place of the hydroxides. The modified cycle becomes:

(1) $Mn_2O_3 + 4Na_2CO_3 \longrightarrow 2 (MnO_2 \cdot 2Na_2O) + 3CO_2 + CO$ at 800°C

(2) $2 MnO_2 \cdot 2Na_2O + water \longrightarrow 2Mn(OH)_4 + 8NaOH_{ac}$ at 100°C

(3) $CO + 3CO_2 + 8NaOH \longrightarrow 4Na_2CO_3 + H_2 + 3H_2O$ at 400°C

(4) $2Mn(OH)_4 \longrightarrow Mn_2O_3 + 2H_2O + 1/2 O_2$ at 800°C

With the first reaction one could benefit from the higher free energy of carbon monoxide formation with respect to carbon dioxide at high temperatures.

We have tested the reaction between Mn_2O_3 and alkali carbonate at the maximum temperature allowed by the evaporation of carbonates (800°C) with various stoichiometric ratios, but again we did not observe any reaction. Even when manganese metal was reacted with carbonates, the maximum valence state attained was 3, and the valence 4 is attained only in oxidizing atmosphere. In this case, however, only CO_2 is formed, and a cycle cannot work under these conditions.
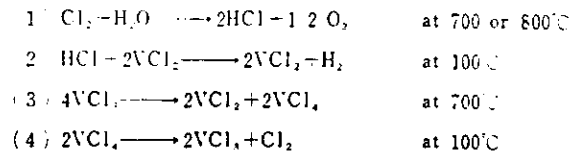
It should be stressed that both variations of this cycle appear possible on thermodynamic grounds.

Mark-3

Vanadium cycles

A study of the halides of the transition metals led us to conceive a cycle working on chlorine and vanadium. In the meantime we found that researchers of the Allison Division of the General Motors Corporation[12] had already described exactly this same chemical cycle as being the most promising one among a group of four in which Ta, Bi, Hg and V are respectively the working elements, together with chlorine.

The reactions for the vanadium cycle are the following:

1. $Cl_2 + H_2O \longrightarrow 2HCl + 1/2 O_2$ at 700 or 800°C

2. $HCl + 2VCl_2 \longrightarrow 2VCl_3 + H_2$ at 100°C

3. $4VCl_3 \longrightarrow 2VCl_2 + 2VCl_4$ at 700°C
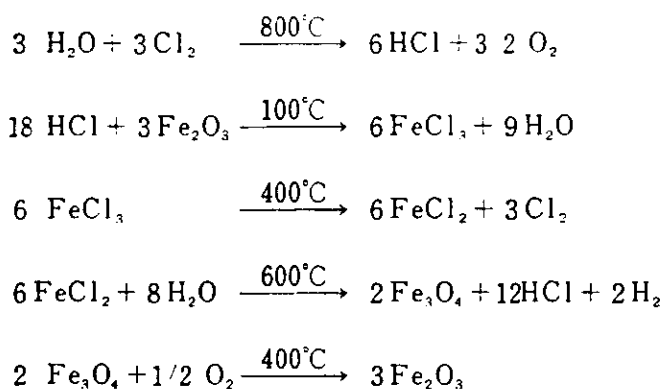
4. $2VCl_4 \longrightarrow 2VCl_3 + Cl_2$ at 100°C

The first reaction of this cycle is industrially well-known. The available thermodynamic data for the vanadium chlorides allow an acceptable yield for each reaction at the temperatures indicated. Little experimental work was done at the Allison Division on Reaction 2. They tried in fact to react VCl_2 with gaseous HCl. In spite of the expected favorable equilibrium they didn't find any evidence of a reaction taking place.

We have planned to do some work on the reactions involving vanadium chlorides, to find more favorable conditions.

The Mark-7 cycle

Based on the reaction between water and chlorine, another cycle has been defined by Hardy and successfully tested[10]. The hydrochloric acid which is formed in the reaction is transformed in iron chloride, which reacting with water produces hydrogen.

The reactions are the following:

$$3\,H_2O + 3\,Cl_2 \xrightarrow{800°C} 6\,HCl + 3\,2\,O_2$$

$$18\,HCl + 3\,Fe_2O_3 \xrightarrow{100°C} 6\,FeCl_3 + 9\,H_2O$$

$$6\,FeCl_3 \xrightarrow{400°C} 6\,FeCl_2 + 3\,Cl_2$$

$$6\,FeCl_2 + 8\,H_2O \xrightarrow{600°C} 2\,Fe_3O_4 + 12\,HCl + 2\,H_2$$
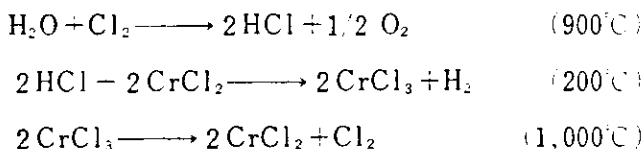
$$2\,Fe_3O_4 + 1/2\,O_2 \xrightarrow{400°C} 3\,Fe_2O_3$$

On the basis of the preliminary experimental tests a flow sheet has been made. A simplified version is given in Fig. 10; the hydrochloric acid circulates in the cycle varying its concentration from 20 to 95% by weight. Calculations made on the basis of this flow sheet give thermal efficiency values ranging from 40% to 45%.
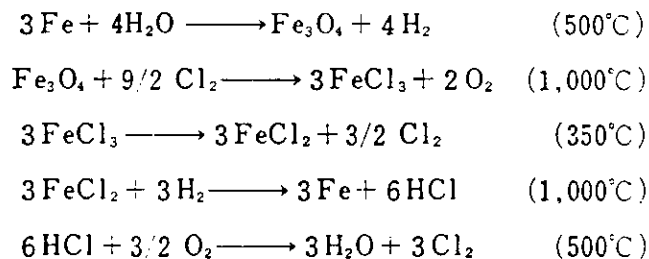
Other cycles

The search for new thermochemical cycles is going on fairly intensively in other places in Europe (e.g. Aachen University, Jülich Nuclear Res. Center) and in U.S.A. (e.g. General Electric, Gulf General Atomics, Atomics International, Institute of Gas Technology). Prof. Knoche of Aachen University is particularly active in inventing new processes.

One of the cycles which has been recently published by him has the special characteristic needing only three reactions:

$$H_2O + Cl_2 \longrightarrow 2\,HCl + 1/2\,O_2 \qquad (900°C)$$

$$2\,HCl + 2\,CrCl_2 \longrightarrow 2\,CrCl_3 + H_2 \qquad (200°C)$$

$$2\,CrCl_3 \longrightarrow 2\,CrCl_2 + Cl_2 \qquad (1,000°C)$$

Another one has the characteristic of including only well-known reactions[13]:

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2 \qquad (500°C)$$

$$Fe_3O_4 + 9/2\,Cl_2 \longrightarrow 3\,FeCl_3 + 2\,O_2 \qquad (1,000°C)$$

$$3\,FeCl_3 \longrightarrow 3\,FeCl_2 + 3/2\,Cl_2 \qquad (350°C)$$

$$3\,FeCl_2 + 3\,H_2 \longrightarrow 3\,Fe + 6\,HCl \qquad (1,000°C)$$

$$6\,HCl + 3/2\,O_2 \longrightarrow 3\,H_2O + 3\,Cl_2 \qquad (500°C)$$

The excessive materials recirculation make this cycle an improbable winner; however it belongs with Mark-7 to a very interesting family of cycles using Fe, Cl and O.

Possible evolution of thermochemical processes

High temperature is a desirable goal because by increasing the maximum temperature at which heat is available:

—The number of possible processes increases.
—The efficiency of these processes tends to increase.
—The processes tend to become simpler: The polar star could be water-cracking with only one step (plus separation) and 100% theoretical efficiency. However high temperatures lead to difficult materials problems and the most probable course in the author's opinion will be that successful processes will cluster in the temperature range between 800° and 1200°C, sticking to more or less conventional chemical engineering practices.

There is still the possibility that eventually water-cracking will be explored by physicists-technologists of the kind that in the Los Alamos National Lab. developed reactors for space propulsion. A crossbreeding of these very high temperature reactors (they have been operated, for short periods, at coolant temperatures up to 2,300°C, the coolant being hydrogen) of plasma and of magnetohydrodynamic (MHD) technology in order to separate the products, might lead to a very sophisticated breakthrough.

The important job at least during the first years, consists in mapping processes. We found a dozen of them, and are aware of another half a dozen invented in other places, especially in the U.S.A. and in Germany. And still many may be possible.

Prof. Knoche at the University of Aachen has developed a logic and set up a computer program to make a kind of preselection of processes that might be thermodynamically possible, releasing the investor from the combinatorial task and concentrating him on the task of evaluating. Although conceive to produce semiworked material this program may greatly speed up the process of exploration.

A complete class of processes we have neglected due to the lack of appropriate organic chemists, are the ones using organic reactions, at least for the colder part of the cycle. But it might be a fertile field especially if one looks for cycles drawing their heat from water reactors, i.e. from heat sources at 300°C, and using more conventional cracking (at around 2,500°C) has a theoretical efficiency of (theoretically 55%).

What are the possible efficiencies?

The thermodynamical treatment of these processes is relatively lenghty, and we suggest to those interested that they consult the excellent papers of Funk[15] and Knoche[13]. It comes out that efficiency is higher than Carnot's essentially because we are not producing mechanical energy, but a chemical with a certain enthalpy and free energy.

Using heat in the range of temperatures available now (500°-800°C) the theoretical efficiency is around 75% (using lower heating value for H_2). Using heat in the range of temperature that can be expected from HTGR's in the next 20 years as a development of present technology (800°-1,200°C) the theoretical efficiency is around 85%. Water-cracking (at around 2500°C) has a theoretical efficiency of 100%, and so the range is given.

Just for the sake of completeness one could say that, conceptually, efficiencies higher than 100% are possible with heat sources above 2,500°C but clearly the fact has no practical importance.

The actual efficiency that will be reached is a matter of luck and ingenuity. Probably the situation is more favorable than in the case of a power station because chemical reactions have less limitations than rotating machinery. To give an example a computer simulation of our latest version of a Mark-1 plant, with fairly realistic conditions, gave an efficiency of 55% or nearly 80% of the theoretical value.

High efficiencies are important for two reasons:

—the obivous one of saving heat laboriously produced.
—the more implicit one, that inefficiency appears as waste heat.

Now waste heat can be considered as a pollutant, or may

just be difficult to dispose of in a plant that naturally tends to become gigantic; in both cases it may strongly limit the number of possible sites for the plant.

What may be the alternative routes?

A conceptually interesting route has been proposed by Gough[16]. The very hot plasma of a fusion reactor ($> 10^6°C$) is injected with aluminum atoms which are excited and emit ultraviolet light. This light passes through steam which is photochemically decomposed into hydrogen and oxygen[16]. The temperature is kept low enough to prevent recombination so that the gases can be separated e.g. cryogenically.

The system has a very good potential at least from a physical point of view, i.e. there are very little thermodynamical limitations to very high efficiency and the plant might come out very simple.

The main drawback is that it demands second-generation fusion reactors, where energy comes from the reaction $D + D = He^4 +$ energy in the plasma, so it should be kept warm for the years 2000's.

Other possibilities have been cursorily investigated, e.g. processes where the water molecule is broken partly thermally, partly electrolytically[12]; or processes where the final product is ammonia.

The processes of the first kind are probably bound to stumble on the same stones as straight water electrolysis. The second kind instead may lead to very interesting possibilities, because the process requires less energy and might be simpler, and because ammonia, apart from its present market. is one of the candidate "hydrogen carriers" to fuel cars. Clever chemical engineers may even find a way to make methanol react CO or CO_2 with ammonia.

What are the alternative primary energy sources?

Apart from nuclear reactors especially designed for the purpose e.g. producing very high temperatures. and fusion reactors that still fall in the nuclear category, the other two primary energy sources that present themselevs to the mind are solar energy and geothermal energy.

Solar energy properly concentrated may be very suitable to run a system of the kind of Mark-1 as single-stage concentrators of proper design may produce a 900°C heat source. Processes taking advantage of the fact that this energy is in form of light may also be devised. For instance a phosphor piling up photons and discharging ultraviolet light of proper frequency may bring to a closer reach Gough's idea of steam photolysis. Chlorophyl e.g. already does something of this kind.

For geothermal energy there are two drawbacks:
—For the time being, temperatures do not appear interesting e.g. less than 250°C, as in the case of the geothermal stimulation project studied in Los Alamos.
—Localized power appear too small by two orders of magnitudes.

It is clear that many lines can connect two points. To sort out the straight one will cost much thinking and sweat. But the reward for the winner is immense: abundant, clean, cheap energy and a $100 billion market to start with.

4. The Consequences

The structure of the potential market

When we first started thinking of hydrogen as a potential candidate as a "vector" for nuclear energy, in a sense

parallel and analogous to electricity, we divided the energy market into various large blocks: Ore reduction, transportation, home etc. and started analyzing the applicability of hydrogen to each sector.

Sieving the pertinent literature we found that in every sector, for special and intrinsic reasons, somebody had thought of using hydrogen and in many cases work was continuing. Just to give some examples referring to the most important blocks:

—in the case of iron ore, the reduction with hydrogen to sponge iron was pursued to take advantage of very special local conditions in view of alleviating the consequences of the increasing prices of metallurgical cokes,
—in the case of ground transportation, the driving force was the possibility of modifying existing cars to make them nonpolluting with only minor modifications,
—in the case of air transportation, the unique lightness of LH_2 plus the possibility of using it as a heat sink in supersonic planes, held the promise of more efficient and cheaper air transport,
—in the case of home usage, American gas utilities had sponsored an "All gas house". Methane being a fairly unreactive molecule the natural gas was converted to produce hydrogen in order to adapt it to the fine requirements of a home, e.g. for catalytic burning. lighting. and producing small amounts of electricity in a fuel call. So a "Hydrogen house" was in fact born.
—in the case of food, the possibility of using electricity from solar cells to make hydrogen and oxygen by electrolysis and using these gases to run a "food machine" for astronauts, was the driving force to study the cultivation of hydrogenomonas for the production of proteins and other nutrients.

All that it clearly very important because:

—it shows that hydrogen has intrinsic advantages for many applications.
—nuclear hydrogen will find the market ready. just as nuclear electricity did.

Let us pass now in brief review such new applications. The pertinent literature is quite spread in time. but due to the increasing interest in hydrogen. some of them have been described in great detail at the 163rd National Meeting of the American Chemical Society in Boston (April 1972) and at the 7th Intersociety Energy Conversion Engineers Conference in San Diego (IECEC September 1972). The proceedings of these conferences are very interesting reading as they sum up much of the work in this field currently being done in the United States.
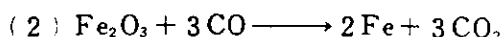
Iron ore reduction

This subject is taken first because steel-making will probably be among the first to profit from "nuclear hydrogen", and also because it will be a large customer.

The reduction of iron ores to produce sponge iron. by the overall reaction:

$$(1)\ Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$
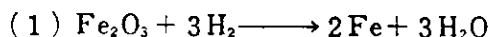
alone or in conjunction with the reaction:

$$(2)\ Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

is a well studied subject. Various commercial processes exist e.g., H-Iron[18], HyL[19], Purofer[20] also numerous plants have been built[21] most of them, however, relatively small.

As a rule of thumb, the amount of hydrogen needed to produce by direct reduction 1kg of iron is roughly one cubic meter. That makes the arithmetics of assessing the size of the market exceedingly easy.

The direct reduction brings the craft of iron-making back to the origins. The Hyttites and the Egiptians, in fact, didn't have furnaces hot enough to melt the iron, so the minerals were reduced by the hot CO and probably H_2 coming from the partial combustion of charcoal. The product was sponge iron that was later consolidated and densified by hammering.

In the modern version the iron ore powder is preferably reduced in a fluidized-bed reactor at temperatures between 500°C and 800°C, depending on the particular scheme. As the first reaction indicated is slightly endothermic, and the second one fairly exothermic in the range of temperatures considered, in some processes a mixture of CO and H_2 is used to obtain athermicity.

Since these processes are quite easy to visualize for a chemical engineer, and the literature quoted is quite informative we will not delve in further details.

The perfection of the blast furnace technology, the amount of capital invested and the economy of scale being still in an evolutionary phase today, make it very difficult for new processes to gain a foothold on a world basis, even if they are more profitable on paper or at the pilot plant stage.

But the rising trend of prices for metallurgical cokes, the introduction of antipollution measures and the reduced development potential of the blast furnace, will be powerful incentives to turn to other processes. The ones based on hydrogen, mixed perhaps with CO, appear most promising in the long run.

It is clear that H-Iron or one of its variants, like the HyL or IRSID sponge iron process, fit best a hydrogen economy, because they use pure hydrogen as the reductant. But if more complex direct reduction systems, using a mixture of H_2 and CO, as in the Futakushi process, appear more favourable, it is very easy to adapt them to pure hyrogen source. In fact the CO_2 in the exaust gases may be brought back to CO by using the water shift reaction backward.

Just to give an idea of how nuclear reactor sizes and steel mill sizes match together, we estimated that a commercial HTGR of 2500 MWth, plus an associated thermochemical water splitting plant of the kind of Mark-1, would produce enough hydrogen to feed a 3.5 million ton/year sponge iron plant.

Such a technique, dissociating the problem of iron ore reduction from that of fuel procurement, could greatly change the geography of iron-making. A reduction of the ore at the mine, with the commercialization of a semi-worked "raw iron" to be elaborated elsewhere, would roughly reduce by a factor of two the materials to be carried around.

Ground transportation

The car is a very important item in the mind of people and it is the basis of a very important industry, so great concern comes from the fact its engine is an important source of pollution. A very simple solution would come from the use of hydrogen as the fuel. The combustion products, water, very small amounts of nitric oxides, traces of unburnt hydrogen, would pass the most stringent antipollution rules (Fig. 11).

Hydrogen engines are not new. Already in 1927 the Zeppelin Company had I.C. engines adapted to burn hydrogen. The objective was to make use of the hydrogen normally vented by the airship to control its altitude. These engines were successfully tested in 1928 in a trip across the Mediterranean. Other types of engines were adapted to hydrogen in the following years both for civil and military purpose, e.g. Erren developed reliable diesel engines working on hydrogen-air or hydrogen-oxygen. A fascinating account of these early developments is given by Weil[22].

The engine can remain essentially the same or with minor modifications in some cases. The Wankel engine is particularly suitable. In our opinion the most appealing solution, just to take one out of the bunch, is that developed by Schoeppel at the University of Oklahoma[23]. Hydrogen is simply injected in the cylinder through a small hole in the spark plug, at the end of the compression stroke. Such a system has the great advantage of leaving the engine completely unmodified, so that a dual fuel system with hydrogen in town and gasoline outside is easy to apply. This feature is a very useful one, because the real problem of the hydrogen car is in the tank: carrying an amount of hydrogen giving the same range as a tankful of gasoline is in fact a tough problem to solve.

The most promising routes are:

LH_2: It has three times the volume of gasoline for the same energy content. It must be kept at 20°K. Dewars with proper characteristics (boil-off < 1% per day) already exist[24]. It is not an easy system to start with, but it is inherently simple and static. It holds a long-term promise. It must be pointed out that, before taxes, the present cost of LH_2 and premium gasoline in the U.S.A. are practically identical for the same energy content[24], [25].

NH_3: Liquid ammonia has a pressure vs. temperature curve similar to propane and it might be carried in bottles as many cars do now with propane. An ammonia cracker is required. The new low-temperature catalysts for ammonia synthesis[26] could lead to a realistic low-temperature cracker taking the necessary heat from the car exaust. Combustion engines can be operated with ammonia as a fuel[27], but pollution reappers under a different disguise.

Metal hydrides: In particular MgH_2 [28], [29], [30] (Fig. 12). They decompose releasing hydrogen, or are reformed adsorbing hydrogen, according to the hydrogen pressure above them (Fig. 13). They can hold hydrogen at densities higher than LH_2. The carrier metals tend to be heavy[29].

Gas cylinders: This is a really proven technology. There are 40,000 cars in Italy only, running on methane carried in cylinders. But hydrogen is about three times less energetic, per volume, than CH_4. So the ranges become too short. Very light gas cylinders made of fiber-reinforced resins and metal liners[31] could greatly improve the situation both from the point of view of volume and weight. Gas cylinders could be the first step in carrying hydrogen for nonpolluting cars for town service. In country roads the car could be switched to gasoline.

Details on hydrogen cars and hydrogen tanks can be found in the literature on this subject, essentially American[22], [23], [32].

The problem of a viable hydrogen car is a very important one, because:

—cars and trucks use from 10% to 20% of the gross energy budget, in developed countries,
—pollution from cars and trucks is becoming a very real problem in densely populated areas, and
—gasoline is an expensive fuel, and "chemical hydrogen" prices are competitive on an energy basis[24], [37]. This means that this market would be economically accessible very soon in an expanding hydrogen economy.

Air Transportation

This is a very interesting field for three main reasons:

—it tends to use the best in available techniques,
—It puts a great premium on weight, and
—takes an increasing share of the energy market.

For the same energy value LH_2 is 2.5 times lighter than jet fuel but unfortunately three times bulkier; LH_2 is also an excellent heat sink that can be used to cool the air-frame and the engines.

These properties have lured aircraft designers for a long time[33], [35], and for the past twelve years NASA has sponsored design and research work on supersonic planes that should reach speeds up to mach 8; they have an aluminium alloy fuselage and relatively low sonic boom [34], [36], [35]. (Fig. 14—Fig. 15).

The U.S. Air Force has already tried successfully LH_2 fuel using a B-57 with wingtip LH_2 tanks. Lockheed has assessed (with very encouraging results) a commercial airplane with large wingtip LH_2 tanks.

The complex details of this subject are well described in the quoted literature. We wish to draw your attention to three particular points:

—The fuel carried by a commercial airplane is three to four times larger than the payload. Therefore, the driving force toward lighter fuels is clearly very strong.
—The trend toward higher speeds makes LH_2 compulsory. Above mach 3.5 LH_2 is the only effective fuel.
—Pollution at take-off and landing could be taken care of right now by using relatively small wingtip LH_2 tanks. This might be a fairly simple and evolutionary way to introduce the LH_2 technology, with a limited but very useful task, and without stringent economic restraints.

Hydrogen in the home

Historically speaking the first large customer for hydrogen has been the home. Many cities in the last century had "gas works" producing in various ways a mixture of CO. H_2 and inerts that was piped to the homes for cooking. lighting and heating

Depending on the manufacturing method. the hydrogen content of this "town-gas" did vary roughly from 50% to 80%.

Presently town gas has been almost completely replaced by natural gas, i.e. methane, but it is on the way to taking a most astute revenge.

A group of American gas utilities and pipeline companies is actually financing a $50 million target project for realizing among other things an "all-gas home", a kind of counterpart to the much-publicized "all-electric home".

Now the quite unreactive methane molecule is not very suitable to many home appliances where energy must be applied in a fine and precise way. So the idea came out to reform the gas right at the house and distribute it essentially as H_2 (eventually diluted with some CO_2)[39], to take advantage of the high reactivity and flexibility of hydrogen.

This "all-hydrogen home" idea is being developed mainly at the Institute of Gas Technology, in Chicago. It works the following way:

—Lighting is made via a phosphor spread on the inside of an open tube, very similar in appearance to a normal fluorescent lamp. Small amounts of hydrogen coming in contact with the phosphor combines with oxygen from air and excite a bright luminescence in the phosphor (candoluminescence)[40]. The operation is cold.
—Heating is obtained by diffusing hydrogen through (decorative) panels made of porous plastics or wood, and impregnated with a proper catalyst. Hydrogen combines with oxygen and the panel constitutes a distributed and even source of heat[39].
—Cooking trays follow the above principle, but use porous metals or ceramics. The trays are flameless, intrinsically safe and lend themselves to a fine regulation[41].
—Cooling can be made with absorption refrigerators, using again a catalytic burner as the heat source.
—Electricity which is still needed, to run at least the vacuum cleaner, is produced by fuel cells. This is an item still under development; many fuel cells exists, but a simple one, sturdy, cheap and capable of unattended operation for many years, is not easy to make[39].

Summing up the situation, hydrogen can take over easily all the energy load of the home, with some problems still for the hard core of electricity consumption. The home and affine commercial uses account for 20%-30% of the primary energy consumption. It is a very "diluted" market requiring a capillary distribution net, but it is a rich and a large one.

Production of food

A turning point in human history occurred with the discovery and invention of agriculture, at the end of the neolitic age. Agriculture, with respect to hunting and gathering, gave rise to higher yields per unit surface and per unit manpower, leading to a surplus of food in a small area and thus permitting a significant fraction of society to concentrate on specialized arts and crafts in systems of strong communication coupling: the towns.

Since then agriculture has spread widely, but as a whole has improved relatively little. On the other hand human population is growing fast and not only is moving to overshoot available agricultural resources, but also occupying for other purposes valuable agricultural land. The privileged position of agriculture comes from the fact that chlorophyl links the biosphere, and us, to the primary source of energy: the sun.

Now, as we said, the basic and revolutionary discovery of our century is a primary source of energy independent of the sun. If we find a lnik between the biosphere and this new source, chlorophyll and agriculture are going to lose their privileged position and the corresponding limitations are likely to fall. Hydrogen can be the link.

Actually a certain number of microorganisms are able to use hydrogen as a source of energy and a reductant and thrive on a completely inorganic substrate: e.g. Hydrogenomonas, or Clostridium aceticum. The source of carbon is CO_2 in both cases[42]. Hydrogen's free energy is used in quite an efficient way to synthesize all sorts of things necessary to build and run the biological machinery, such as proteins, vitamins, carbohydrates (or alternative energy storages). The energy conversion efficiency—i.e. energy in organic products to energy in hydrogen—is quite high and of the order of 50%. On the other hand the multiplication rates of microorganism, are exceedingly fast; the biomass has doubling times of the order of hours.

Now the average man needs a caloric input of 2500-3000 Cal/day, corresponding to a rounded mean power of 150W. Taking into account all the losses from nuclear energy to hydrogen, and from hydrogen to food synthesized by microorganisms, to have 150W "at the mouth" one should count on roughly 0.5-1Wth at the reactor level. This means that our famous 2500MWth HTGR, may be the primary energy source to feed a few million people.

At the Institute of Microbiology at the University of Göttingen under the direction of Prof. Schlegel research on the production of proteins for human consumption, using Hydrogenomonas, is presently going on. As monocellular organisms tend to be too rich in nucleotides for a balanced human

diet, the idea they are following is to make the Hydrogeno-monas "secrete" extracellular proteins. Just as a cow secretes milk. This, via proper selection, may permit the production of selected proteins tailored to their final use.

Apart from the selected proteins for human consumption, the biomass would probably be used to feed efficient "converters" like poultry, transforming them into chicken and eggs. This is not to say that man will start feeding over night on monocellular food and that agriculture is bound to disappear overnight. But this possibility is philosophically appealing and in any case very comforting.

Chemical Hydrogen

The world production of hydrogen reaches today 20×10^6 tons/year, roughly equivalent to 200 billion Nm^3. Half of it is used to make ammonia. About 30% goes into refinery processes (Table 1).

The last use is growing very fast because:

—Hydrocracking and hydrotreating processes are increasing in importance,
—hydrodesulfurization of fuels is being made compulsory to reduce pollution, and
—demand for substitute natural gas (SNG) is increasing.

Aside from the global size of the hydrogen market, two characteristics make it very important to us. These are:

—The size of the plants is large enough to accomodate the production of a water-splitting plant associated to a full-fledged HTGR. For instance, our famous 2500MWth HTGR could feed a plant producing about 1.6 million tons NH_3/year, probably a medium-size one in the next decade.
—The price of chemical hydrogen is three to four times higher than the price of fuel, for the same caloric value.

A most probable evolution of this market in the next 30 years will be that ammonia production will reduce its pace of growth, and that the growth in hydrogen production will be essentially supported by SNG production. Since the new sources of natural gas, in Alaska, Siberia, Australia, and in the North Sea, are fairly small compared to projected NG consumptions in the next decades. a large amount of gasification, in the hundreds of millions of tons/year bracket, may be expected, especially if an independent source of relatively cheap hydrogen comes up.

Hydrogen is the key to gasification; each ton of coal requires about 300kg of hydrogen for its gasification to SNG and a ton of oil about 150kg. As our famous 2,500 MWth HTGR is expected to produce about 350,000 tons H_2/year assuming 50% efficiency, it could support the methanization of half a million tons of coal/year or of one million tons of oil. These figures are clearly only orientative.

Hydrogen distribution and storage

The first objection raised in any discussion of the distribution of large quantities of hydrogen is that air hydrogen mixtures are explosive. This is true, but it is equally true that methane/air and hydrocarbons/air mixtures are highly explosive and do cause considerable death and destruction every year; yet this does not slow down the growth of consumption of these fuels, even at the expense of others, such as coal, which are far less explosive-prone but dearer and less easy to handle.

Incidentally, when the first motorcars appeared, the danger represented by the various dozens of liters of gasoline in their tanks was regarded as so prohibitive that in England they had to be preceded by a man on foot waving a red flag—a precaution which would certainly be more useful today,

though for other reasons.

The fact is that the question must be tackled with a healthy sense of the hazards involved, and the answer found through empiricism and technology. We are therefore very glad to show in Fig. 16 a network of hydrogen pipelines linking various firms in Germany with large-bore pipes and an overall length of about 300 kilometers. Similar networks exist in the United States, notably in Texas, as part of more complex systems for carrying chemical intermediates between refineries and petrochemical works.

The other point to make is to evaluate how much this transportations will cost. We have made an orientative study with the help of SNAM, the Company that distributes natural gas in Italy, in orler to see the effect of the physical properties of hydrogen on the characteristics of an optimized pipeline[43]. The results are summarized in Table 2.

The following three points deserve attention:

—Optimum pipe size tends to be larger than for natural gas, for the same energy transported.
—Pumping stations tends to be much more distant than for natural gas.
—The optimized cost of transporting energy is not substantially different for the two cases. especially if we take account of the fact that hydrogen pipelines will eventually carry more energy.

Our optimization is for the moment only partial and geared to local conditions. So we can expect further improvements. The fact that pumping stations are so far apart has the important consequence for relatively small countries such as Western Europe or Japan that hydrogen needs to be pumped only at the source. For that reason in our Mark-1 process, we are studying the conditions for obtaining high-pressure hydrogen right from the reaction producing it and so avoiding any pumping at all. If hydrogen has to be transported overseas; the analogy with natural gas suggests liquefaction and cryotankers, but other improbable systems may still emerge, as for example that of using blimps[44].

The largest experience in making and transporting LH_2 can be found in the U.S.A. due to the very large amounts of LH_2 used as propellant in rockets[45] [46]. It is stored in spherical containers up to about 5.000 m^3 (Fig. 17). Containers up to 50,000 m^3 could be built without further basic development[47]. Boil-off due to the heat flowing in through the insulation. is a few parts per thousand/day. These data are important especially because they show that the basic technology exists to build large sea tankers.

People in the U.S.A.[48] have given some consideration to piping hydrogen as a liquid. At the present stage of technology this method does not appear to be competitive. It might become so for certain special cases, e.g. if hydrogen is transported by sea and is already in liquid state. One would then have the extra advantage of having it liquid at the terminal point for easy storage. Or if cryogenic cables for transporting electricity would follow the same route and share the cost of the installation[48].

Liquid hydrogen being routinely transported with road trailers, railway wagons and barges[49] [59] (Fig. 18) might at the end be the form which will accepted as a fuel for vehicles. This may be another incentive to transport it as a liquid in the trunk lines, especially if it starts as a LH_2 arriving by sea.

The storage of hydrogen can strictly follow the practice of natural gas storage:

—The pipelines, by allowing changes in pressure. already constitute an important capacity (hours).
—The acquifers can be used to hold gas "bubbles" with enough capacity to take care of the peak load of a town[51].

—Caverns have been leached in salt domes with gas capacities in the range of $100 \times 10^6 Nm^{3(52)}$.

—Exhausted gas fields can be used to store hydrogen and the capacities can be very high. The Groningen gas field in Holland, could contain enough hydrogen to satisfy all energy needs of Western Europe for a few years.

The argument that with respect to methane the hydrogen molecule being lighter is more "leaky" is somehow weakened by the fact that it is also less energetic. As a first approximation the energy leakage is equivalent.

Hydrogen and electricity

The fact that hydrogen can:
—be carried over long distances cheaply and unobtrusively in buried pipes,
—be stored underground,
—be transformed in various ways into electricity

has much stimulated the imagination of people in the electric utilities, plagued by siting problems, ecologists and peak loads[53] [54].

The paper given by Hausz et al. of TEMPO General Electric at the IECEC 1972[55] represents perhaps the most thoroughly elaborted specimen of these considerations. Hausz analyzes the economical consequences of a pipeline grid distributed all over a region or a country, hydrogen and oxygen produced at a remote site. Electricity would be locally generated by fuel cells or by relatively small gas-steam turbine generators, a kind of internal combustion steam engines. Both are capable of ultimate high efficiencies (up to 60-70%). Rejected heat would be distributed locally following the concept of the total energy system (Fig. 19).

On the size of the plants

From the viewpoint of internal economics of the plant, the larger the better, as generally is the case. For the first installations, if the hydrogen plant captive to an ammonia plant, the size will be determined by a balanced optimization. It will be large enough however to use the bigggest reactors available[56].

When a distribution hydrogen-net is set up, linking many producers to many consumers, then the problems encountered in electric grids, when properly interpreted, can give some good indications. For instance: one of the conditions generally respected in an electric grid is that the power of a station should never be higher than 10% of the power of the economically connected grid. This is because in case of failure of one station the system, by stretching a bit, can take up the load. The interesting counterpart of this condition is that since Edison's time the size of the power units did double every seven years in neat accordance with the fact that the "intensity" of the grids did double every ten years, due to the increase in electricity consumption, and their extension did double every 15-20 years due to the evolution of power lines.

Now, drawing on the analogy, one has to take into account the fact that electrical energy cannot be stored as such, but hydrogen can, the most obvious and promising system being that of using exausted gas fields for large capacity, and properly adapted aquifers or caverns leached out in salt layers for medium to small capacity[50] [52]. Another point is that transporting hydrogen by pipeline is roughly one order of magnitude cheaper than transporting electricity[43]. To give a feeling of the situation, a 48-inch hydrogen pipeline may carry up 50GW, this is equivalent to the total electric generating power installed in Japan.

The expected consequences are:

—In relatively small countries like Western European ones and Japan, there will be just one grid covering all the territory and perfectly interconnected.

—The capacity of the stores will take care not only of the accidental outage of one or more stations, but also of the daily and seasonal peaking.

—The 10% limit for the size of the simple station can be released.

—The hydrogen stations can work near 100% capacity.

Following the preceding points these stations will tend to become gigantic, the appropriate unit of measurement being in the range of the 100GW. For a long time the only limitation will probably come from the size of nuclear reactors available. This question of size is very important because, when the technology is mature, size has a very beneficial effect on prices. Assuming e.g. the crude but not uncommon relationship $Cost=Size^{0.75}$, multiplying size by a factor of 16 reduces cost by a factor of two. And in the very competitive energy market this may make the difference between night and day.

Strategy of penetration

Once one has solved all the technical problems, one has to go into the arena and be competitive. Most likely our hydrogen will not begin its career as a fuel, because the market for hydrogen as a chemical has the perfect structure for assimilating new technology, and because hydrogen is worth now about three or four times as much as a chemical than as a fuel of the same heat value.

The first customers will most probably be new ammonia plants. They will have the right dimension to use all the production from a hydrogen plant employing an optimum-size commercial reactor and they pay a premium for very pure hydrogen. To best use the by-product oxygen, which is worth almost as much as hydrogen, per Nm^3, at present market prices, the site of this ammonia plant should be near a large steel mill, or an oxygen pipeline (Fig. 20). Heavy water, the second by-product, has no problems of transportation, although a nearby final concentration plant would help in various ways. Selling properly the by-product is extremely important for the first plants, because at current prices they are worth almost as much as the hydrogen. Doubling the gross income of the plant at very little cost evidently is bound to make the crucial first step much easier (Table 3).

Once on the chemical market, even with the crutches of the by-products at first, the conquest of the whole of it, and then of the whole energy market will follow with the logic of a theorem. In fact one of the characteristics of this hydrogen is that its cost is almost purely technological, i.e. a manufacturing cost. The cost of uranium, which is the only mineral nominally consumed, at the present reference price of $20/kg has an incidence of less than 1%. (For a specific HTGR reactor and with actual prices for hydrogen we calculated 0.25%).

Now manufacturing costs decrease according to well-known learning curves which have been put in compact mathematical form[57]. One the other hand minerals in general[58] [59], and fossil fuels in particular tend to rise in cost due to the combined fact that as time goes on ore bodies become leaner, and more expensive to discover. Accordingly it is only a question of time for the descending curve of "nuclear hydrogen" cost, first to become independent of the crutches of the by-products, then to cross the raising cost curves of coke, natural gas, oil and coal.

Since the market can accept very soon very large unit sizes, the effort should go not only to make the processes efficient, but also to direct the technology toward very large plant sizes. In practice the most probable situation will not

be a sudden and integral substitution of a certain fuel, this never happened before, but a gradual intermingle and phase out: the extreme flexibility of hydrogen will make the transition very smooth.

For example:

—In iron ore reduction, the new capacity in steel mills can have direct reduction units to produce sponge to substitute for scrap.
—SNG produced by coal and oil gasification, using nuclear hydrogen, will carry into the classical fuel market the fraction of its energy coming from nuclear reactors.
—Cars able to switch from gasoline to hydrogen may slowly switch to hydrogen only.
—Airplanes with wingtip LH_2 tanks for take-off and landing, may see their tanks grow until they carry all the fuel needed for the entire trip.

It is not unreasonable to think that oil companies will take over this new source of energy and will benefit most from it. They have the capital, the technology, the aggressiveness to do it. After all, a water-splitting nuclear plant is not very different from an oil field.

Uranium procurement

A very pertinent question is: to come out from the problems of fossil fuels procurement, are we not going to fall into the problem of uranium procurement? A very searching study made by Brinck[58] [60] on this subject shows that on a world scale there is no reason to be alarmed. In the current range of costs, reserves range in the billions of tons of uranium (Fig. 21). Assuming breeder reactors, one ton of uranium may be worth one million tons equivalent of oil in the form of hydrogen, and this puts cheap uranium reserves in the high brackets. But these reserves are again not evenly distributed over the earth, and a philosophically more satisfying solution would be welcome.

This solution exists, at least in principle. Seawater contains about 3.4µg of uranium/liter. It may seem little but it is not. Let us take for example a nuclear power station cooled with seawater. The amount of uranium carried by the cooling water is an order of magnitude more than the uranium fissioned in the power station! Now the problem of recovering uranium from seawater has been studied in Great Britain[61] [62] and in Japan[63]. Titanium dioxide appears a promising absorber and the economics of the process are in the correct range if the necessity of constructing large civil works is obviated[62]. The uranium content of the sea is about 5 billion tons.

Conclusion

This rapid journey in the realm of the hydrogen economy leads us to the following conclusions:

—All the energy needed for a technological society can be supplied in the form of electricity and hydrogen.
—The natural trend of technological evolution lies in this direction.
—Hydrogen is the perfect energy carrier from the point of view of the environment.
—Nuclear reactors can be used to produce hydrogen with thermo-chemical processes having great potential for development.
—The sea can be the ultimate source of fissionable material.

We added Table 4 to stimulate imagination. One should never underestimate the power of dream in fostering human action.

Table 1 World consumption of hydrogen (1970)

Ammonia synthesis	about	$100 \times 10^9 m^3$
Methanol synthesis		25
Other chemicals		10
Hydrotreating/desulfurization		30
Hydrocracking		30
Refinery fuel (off-grade hydrogen)		10
	Total	$200 \times 10^9 m^3$

Table 2 Transportation costs for hydrogen and natural gas

Energy Gcal/sec	Type of gas	Optimal distance between stations km	Capital costs $10^6$$/Gcal/sec		Transportation cost $/Gcal/ 1000km	H_2/CH_2	
			Pipelines	Pumping stations		Capital	Transp. cost
1	H_2	500	242	10	1.23	1.44	1.36
	CH_4	150	166	10	0.90		
2	H_2	500	190	10	0.98	1.43	1.40
	CH_4	150	131	8	0.70		
3	H_2	500	163	10	0.85	1.42	1.39
	CH_4	150	114	8	0.61		
4	H_2	500	145	10	0.77	1.39	1.38
	CH_4	200	104	8	0.56		

Note: Length of the pipeline: 100 km · Max. pressure: 65 atm.

Table 3 Orientative economic analysis for the first water splitting plant

Assumptions	
Reactor investment/kWth	$50
Fuel cycle cost/kWth h	0.5mils
Market price for H_2	15mils/m³
„ O_2	12mils/m³
„ D_2O	$60/kg
Operation	8,200hr/year
Efficiency	50%
Gross product value, about	$40
Running costs	
Fuel	$ 4
Operation	$ 2
Capital charges	
Reactor (int. & depr. 16%/year)	$ 8
Chemical plant (int. & depr. 25%/year)	$26
Breakeven investment for the chemical plant	100$KWth

Note: The site is chosen in order to sell the by-products at current prices.

Table 4 Target energy island

Year	1991
Site	Atoll in the Pacific
Reactors	5-10 HTGR + Breeders or HTG Breeders
Nuclear power	1 TWth (10^9kWth)
Efficiency	60% (lower heating value H_2 produced/heat consumed)
Hydrogen produced	500 million tons oil-equivalent/year
Lagoon size	2,000 × 2,000 × 20 meters
Cooling water	500 billion tons/year (500km³) pumped from the deep and warmed up to surface water temperature
Uranium recovered	From sea water (50% effic.) 600 tons/year (dbsorption on Titanium dioxide)
Uranium consumed	In the plant (80% fissioned) 500 tons/year (nongrowing crossbreeding reactor system)
Transportation	Liquid hydrogen in tankers
Investement	10^9 kWth × 50$/kWth = 50 billion $. Includes: on site Uranium extraction, Fuel cycle, Liquefying plant.

Fig. 1 The very tight static link between useful energy and Gross National Product is dramatically shown in this figure (Ref. 64). The dynamics is given in fig. 2.
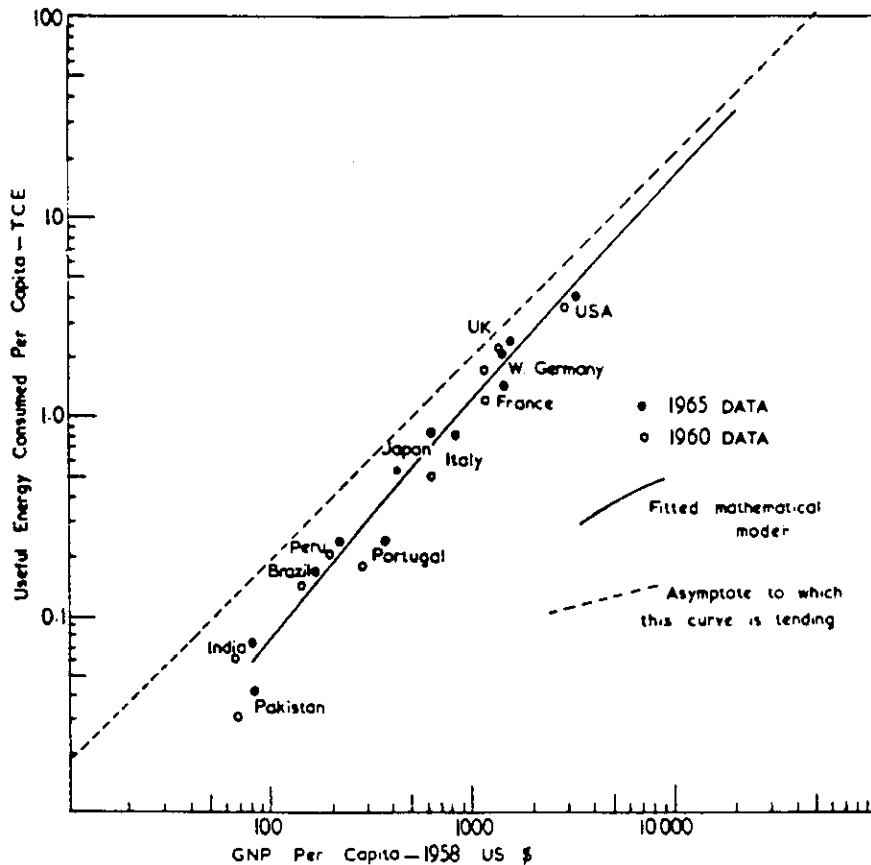
Fig. 2 The fact that Japan is the fastest growing industrial power is reflected in the figures referring to energy consumption. They show also a fast growing problem.

Region	Average Annual Percentage Rate of Change		Percent of World Total	
	1950-65	1965-80	1965	1980
United States	3.0%	3.5%	34.2%	26.8%
Canada	5.1	5.5	2.9	3.0
Western Europe	4.4	4.0	20.0	16.8
Japan	9.9	7.9	3.3	4.9
Middle East	10.2	9.4	0.9	1.5
Other Asia	7.6	8.2	2.8	4.3
Oceania	5.0	4.8	1.2	1.1
Latin America	7.6	7.4	3.5	4.8
Caribbean	8.6	8.4	2.0	3.1
Other Latin America	6.5	5.9	1.5	1.7
Africa	5.4	6.5	1.7	2.0
North Africa	4.6	5.6	0.3	0.3
Other Africa	5.6	6.7	1.4	1.7
U.S.S.R.	7.4	6.5	15.9	19.1
Communist Eastern Europe	5.8	4.6	7.1	6.5
Communist Asia	14.4	7.6	6.5	9.1
WORLD	5.1	5.2	100.0	100.0
Excluding Communist area	4.2	4.7	70.5	65.3

Fig.3 Mark-1 process.
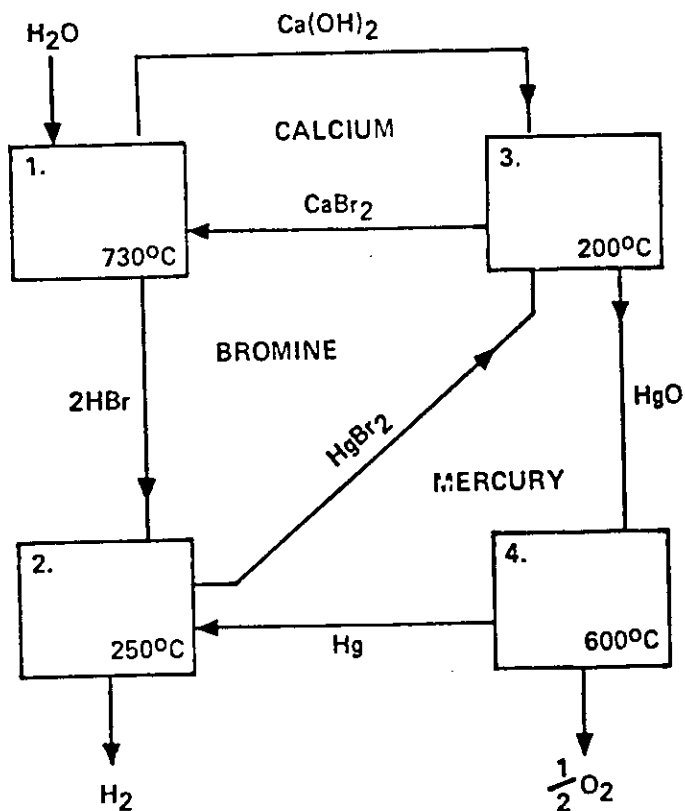
Fig. 4 Hydrolysis equilibrium constants as a function of temperature

total pressure = 1atm

for $T < 820°K$ $K = \dfrac{(HBr)^2}{(H_2O)^2}$

for $T > 820°K$ $K = \dfrac{(HBr)^2}{H_2O}$

experimental

calculated
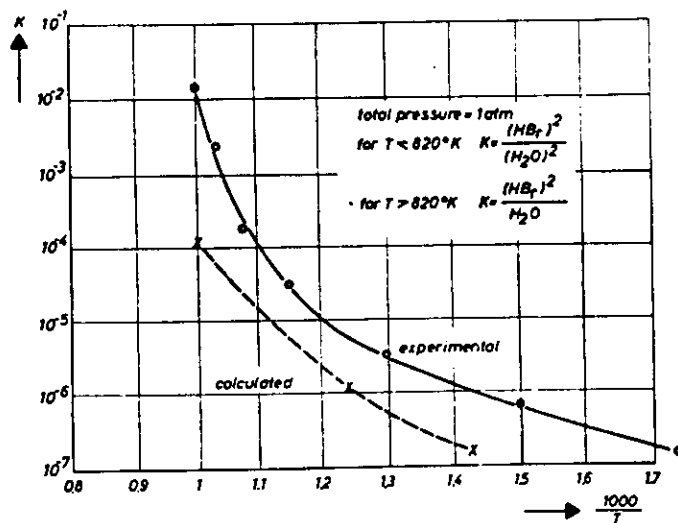
Fig. 5 Ca(OH)$_2$=CaO+H$_2$O—Decomposition
pressures
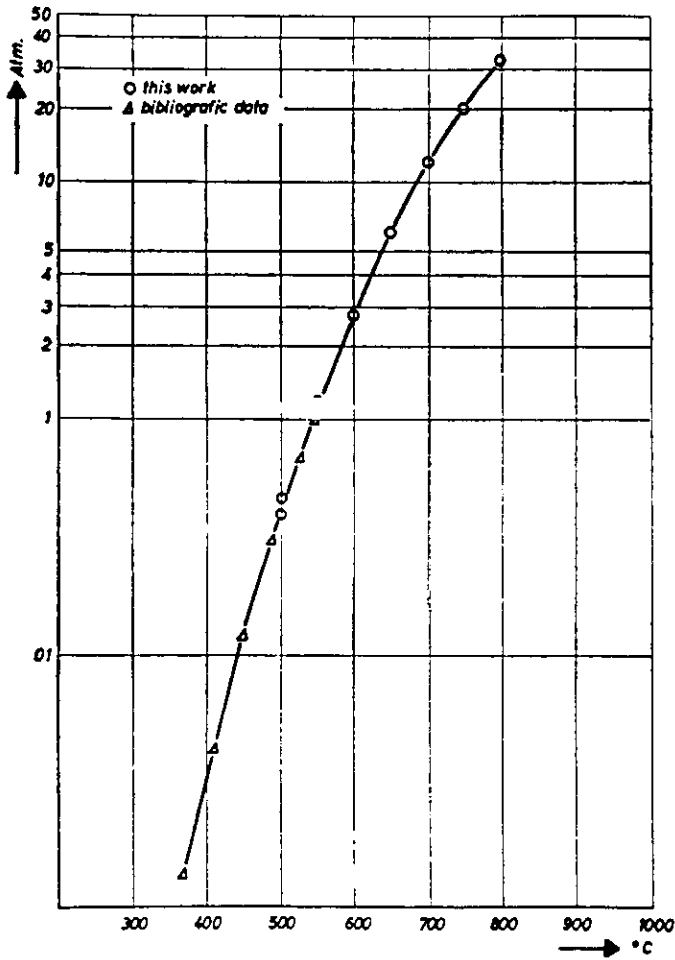
Fig. 7 Hg+2HBr=HgBr$_2$+H$_2$—Hydrogen formation rate
at 200°C Influence of HBr concentration

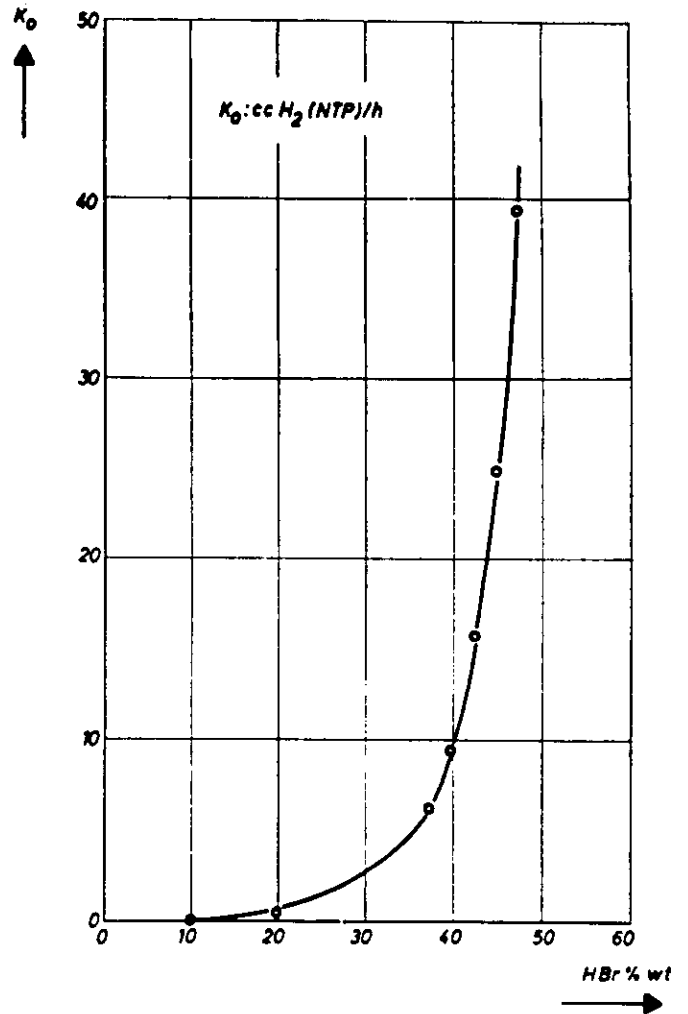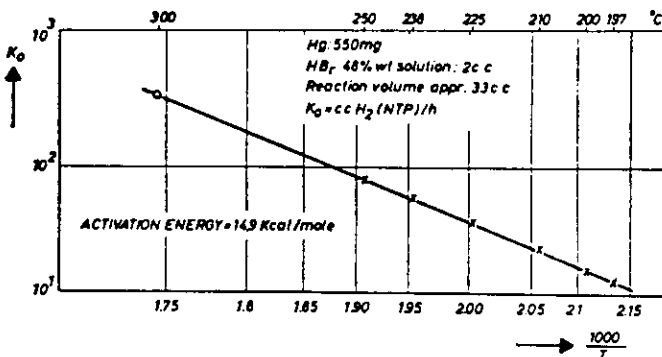Fig. 6 Hg+2HBr=HgBr$_2$+H$_2$—Temperature dependence
of rate constant

Fig. 8 HgO=Hg+1/2 O$_2$—Dissociation pressures

Fig. 9 Mark-1 flow-sheet (HF, heating fluid)

Fig. 10 Mark-7 flow-sheet (HF, heating fluid)
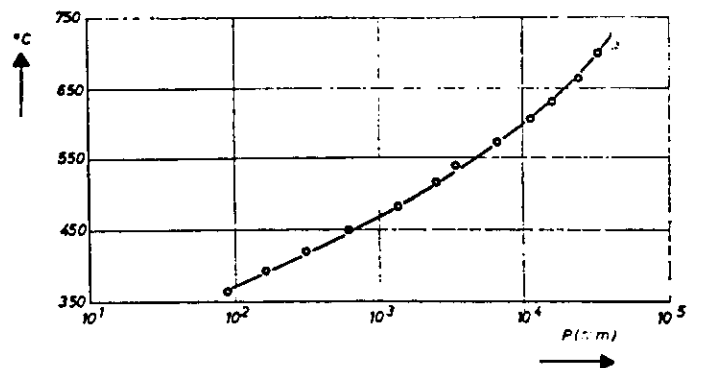
Fig. 11 Nitrogen oxydes from gasoline engines and from "hydrogen injection" engines (Schoeppel)
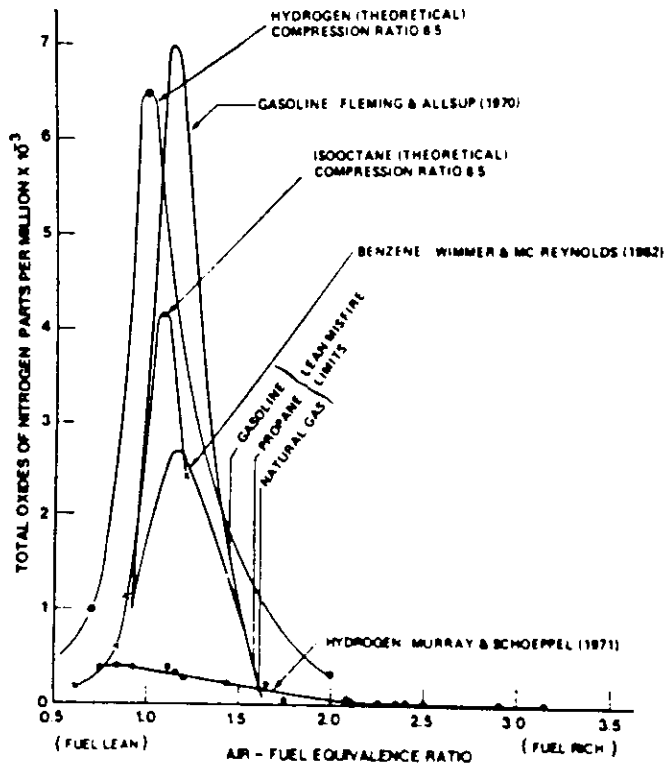
Fig. 12 Equilibrium pressures of H_2 over different hydrides
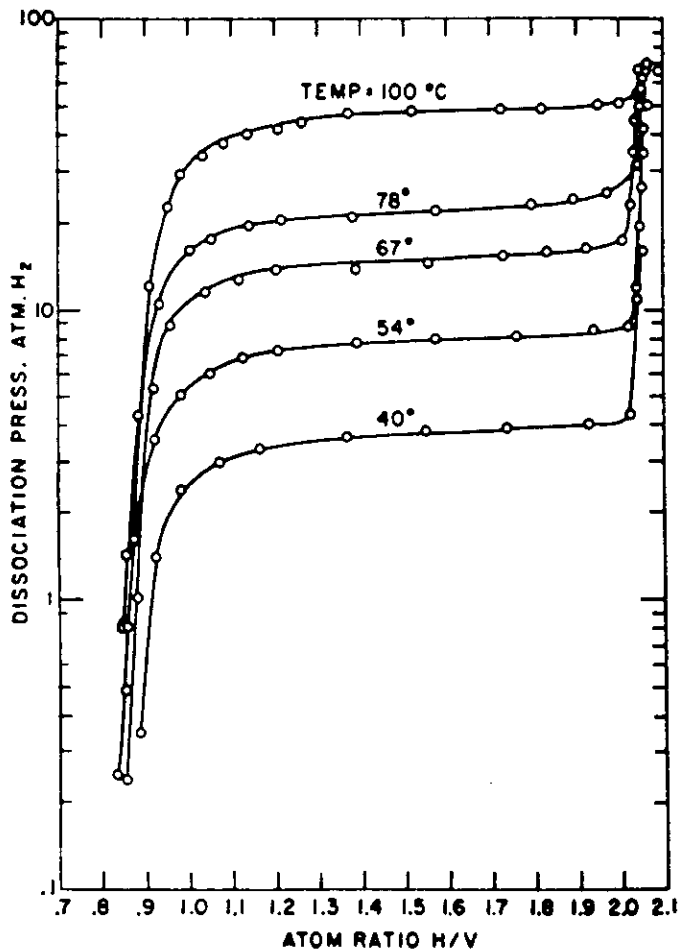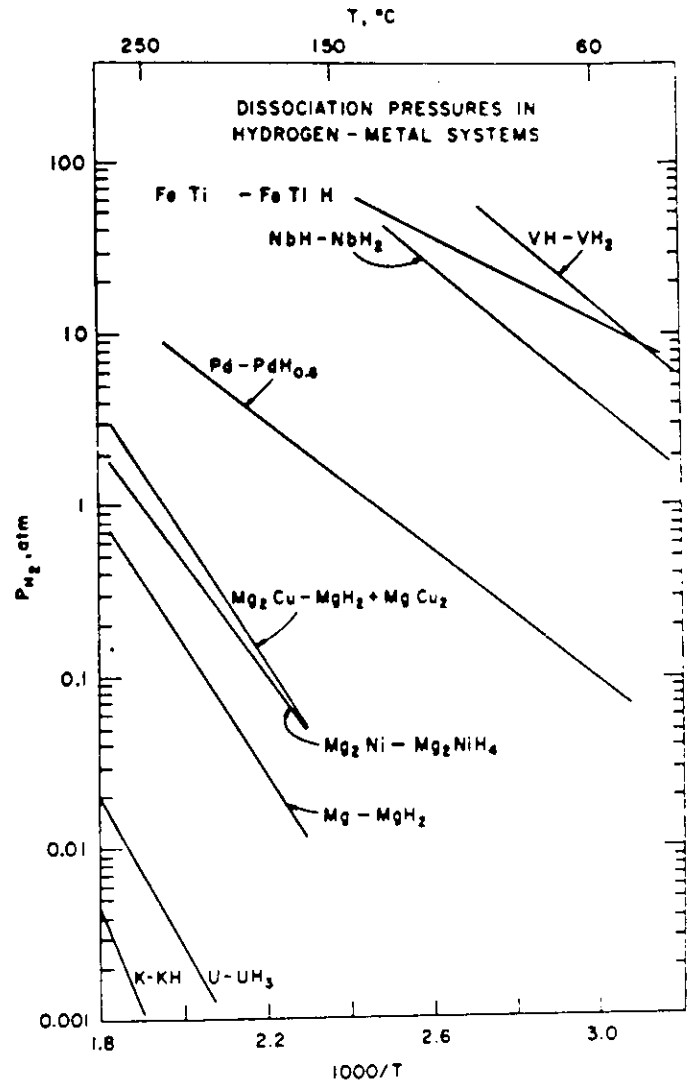
Fig. 13 Typical hydrogen pressures over a metal hydride as a function of fraction of hydride already decomposed (left)

Fig. 14 Sketch of an hypersonic airplane showing the use of the airplane body to produce a shockwave compressing air for the ramjet engines
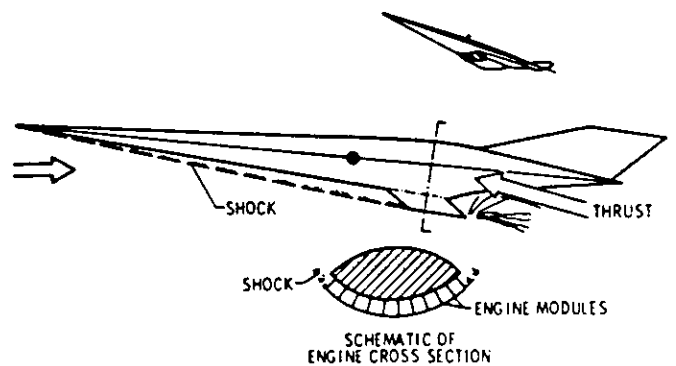
Fig. 15 Trends of LH₂ costs in USA

RELATIVE COST PER Btu OR PER J

LH₂
HISTORICAL
PROJECTED
JP

100, 50, 10, 5, 1
1950 1960 1970 1980 1990 2000

Fig. 16 An hydrogen distribution network in Northwestern Germany. Total length about 300 Km

GEWERKSCHAFT AUGUSTE VICTORIA
PHENOLCHEMIE
RECKLINGHAUSEN
RUHRCHEMIE
VEBA CHEMIE
GEWERKSCHAFT VICTOR
DUISBURG
BAYER UERDINGEN
HOWINOL
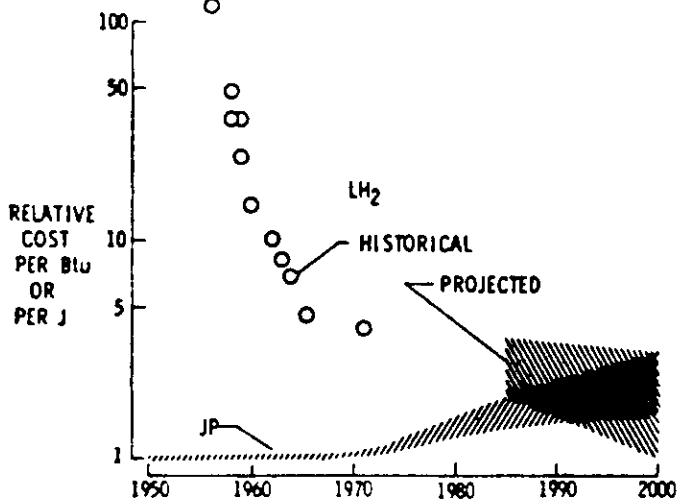ESSEN
MAIZENA
DUSSELDORF HENKEL
BAYER LEVERKUSEN

Fig. 17 Cryogenic LH₂ containers at the Nuclear Rocket Development Station in Nevada
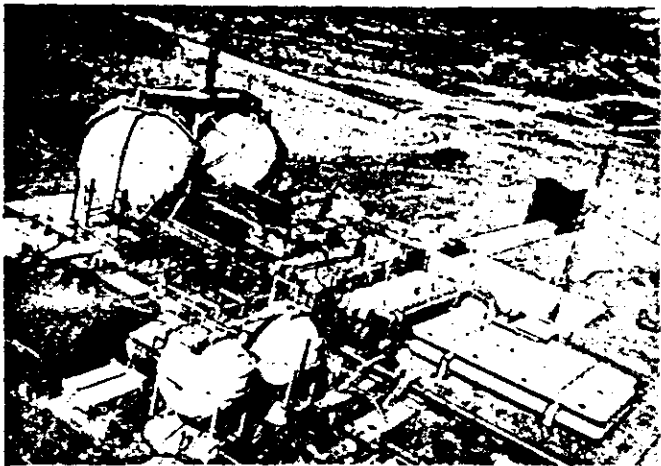
Fig. 18 Cryogenic barges to carry LH₂ and LOX

Fig. 19 An hydrogen economy as seen by TEMPO-General Electric

FUEL
THERMAL SOURCE
DESALTING PLANT
HEAT
BYPRODUCT HEAT
CONVERSION TO HYDROGEN AND OXYGEN
BYPRODUCT WATER
OXYGEN STORAGE
HYDROGEN STORAGE
HYDROGEN FOR: INDUSTRIAL COMMERCIAL RESIDENTIAL TRANSPORT
OXYGEN FOR: INDUSTRIAL MUNICIPAL
BYPRODUCT HEAT
CONVERSION TO ELECTRICITY
BYPRODUCT WATER
ELECTRIC DISTRIBUTION

Fig. 20 An oxygen pipeline in Northwestern Europe
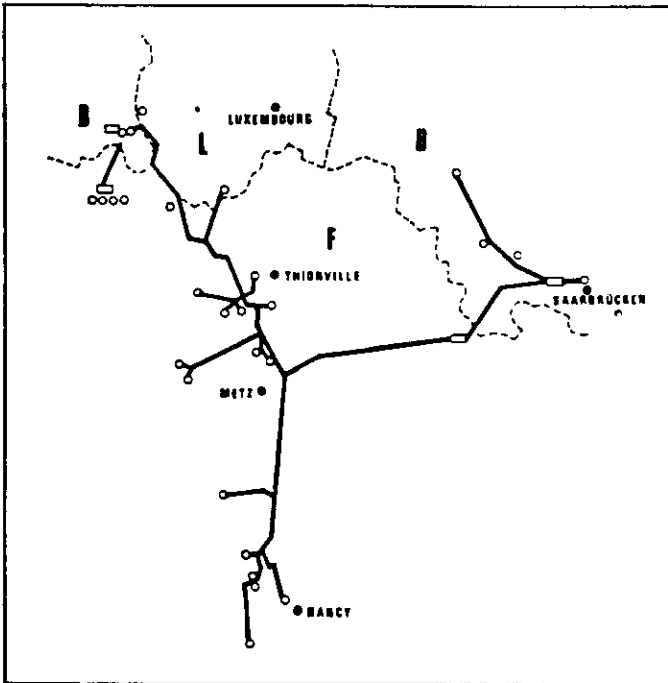

Fig. 20 An oxygen pipeline in Northwestern Europe

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Fig. 21 Forecast for world uranium reserves

Fig. 21 Forecast for world uranium reserves