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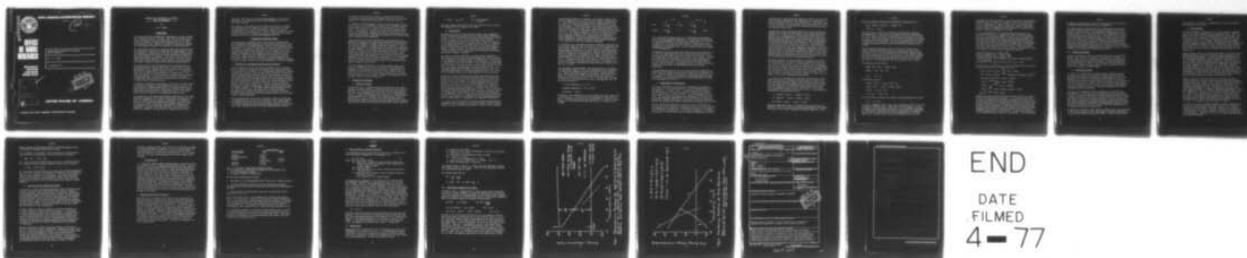
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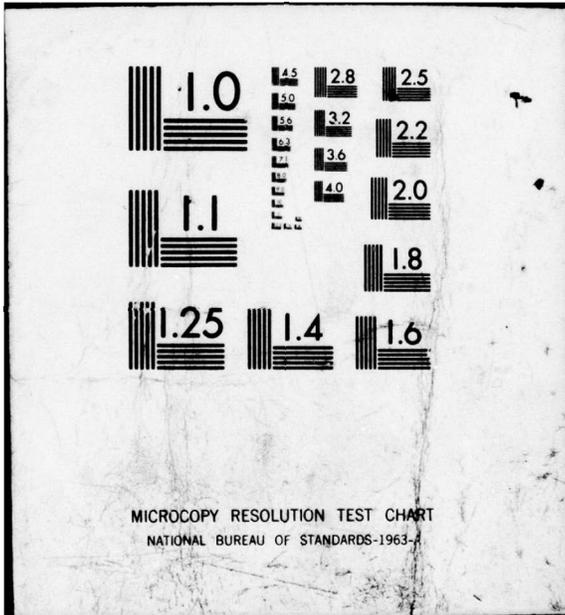
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# ONR LONDON CONFERENCE REPORT

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## OFFICE OF NAVAL RESEARCH

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INTERNATIONAL CONFERENCE ON HYDROGEN AND ITS PROSPECTS
DR. W. G. SOPER
31 DECEMBER 1976

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INTERNATIONAL CONFERENCE ON HYDROGEN  
AND ITS PROSPECTS

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by

W. G. SOPER

INTRODUCTION

The steady depletion of fossil fuel resources is forcing a search for alternative sources of energy. This search includes nuclear, solar, geothermal, wave, and wind energy, as well as the study of ways to utilize the lower grade resources such as oil shale and low-quality coal. Adding to the task is the need to consider the environmental effects of new systems for power generation.

Not only must new sources of energy be found, but techniques must be developed for storing the energy and for transmitting it over long distances. Electricity is now the principal "energy vector" for carrying power from central generating stations, through distribution networks, to consumers. For remote locations and for other cases where connection to a power grid is not practicable (motorized vehicles being the prime example), petroleum products now provide excellent energy storage with high energy density.

This picture will change drastically with the disappearance of petroleum supplies. One may hope that the future will see the development of a new generation of large central power stations that use new energy sources (nuclear, solar, . . .). Electricity, then, will continue to be available as an energy vector. For vehicles, however, we at present have no satisfactory alternative to petroleum fuels. Use of electricity stored in batteries is a possibility (ESN 30-11:497), but present energy densities are far below those of petroleum fuels.

In addition to vehicular requirements, there will be a future need for storage of energy in large quantities at power stations, the purpose being to absorb excess power in low-load periods and provide power to the grid during high demand. Today's power plants suffer from the lack of such a system, and those of the future will be even less capable of accommodating varying loads.

In the search for an energy storage-medium appropriate to the needs described, compatible with future energy sources and possibly superior to electricity as a carrier in distribution networks as well, the gas  $H_2$  has attracted much attention. As a constituent of water it is one of the earth's most abundant elements, and its production can be completely independent of carboniferous substances. Hydrogen is an excellent fuel, reacting with  $O_2$  in the air to produce a very high heat of combustion with little

pollution. While  $H_2$  is not without shortcomings, its successful employment as a high-energy fuel has been demonstrated in the recent space program.

The urgency of the search for new sources and carriers of energy, and the promise that  $H_2$  appears to hold in this regard, provided the motivation for a recent international conference entitled "L'Hydrogene et Ses Perspectives." Held in Liège, Belgium, 15-18 Nov 1976, the Conference featured 42 papers by researchers and program managers from the U.S. and Western European countries.

#### DISCUSSION OF SELECTED PAPERS

This report will concentrate upon those technical presentations at the Conference that appeared to relate most directly to the eventual solution of the energy problem. Omitted from discussion will be papers on (1) plans (in cases where no technical data were given); (2) safety (unquestionably important, but best treated in a separate review); and (3) routine uses of  $H_2$  in industry today. The complete proceedings of the Conference will be available in May 1977 from: Association des Ingénieurs Electriciens, rue Saint-Grilles 31, Liège, Belgium. Each paper in the proceedings will be printed in one of the four Conference languages (English, French, German, or Dutch), and each will have summaries in all four languages.

#### I. Timetable for Introducing New Sources and Carriers

Several speakers reviewed the present estimates of fuel resources with the objective of defining how rapidly new energy sources and carriers must be introduced. M. Van Rysselberge (Laborelec, Belgium) estimated the duration of the world's fossil reserves to be as follows: natural gas and petroleum--two to three decades, bituminous shales and sands--three to four decades, and coal--several centuries. He reviewed as well the estimated resources of fissionable materials and their distribution over the world. No attempt was made to estimate the duration of fissionable resources, in part because the advent of the breeder reactor will increase the energy available by almost two orders of magnitude. Fossil resource estimates given by a later speaker, R. D. Witcofski (NASA Langley Research Center), for the U.S. alone were about half those of Van Rysselberge. Witcofski also included an estimate for the duration of uranium: 25 years without and 1,800 years with breeder reactors, at the 1974 rate of energy consumption.

Van Rysselberge also stated that "renewable" sources of energy are not expected before the turn of the century, solar energy possibly contributing as much as 25% by the year 2025. In a later paper A. B. Hart (Central Electricity Research Laboratories, U.K.) agreed that nuclear energy may not be the only next-generation source.

He believes that ocean wave energy, converted from mechanical to electrical form, and then to chemical form in  $H_2$ , will become important in England in the early part of the 21st century.

An estimate of the development of  $H_2$  as an energy vector in the next 25 years was provided by P. Valette *et al* (SCIENCE, Belgium) who reported results of a survey of 86 authorities in 13 countries. They expect  $H_2$  to carry 5% of the world's energy requirement in the year 2000. By then they expect also that half the  $H_2$  will be produced by decomposition of water (as opposed to virtually none at present), and that nuclear plants will provide about half the energy for  $H_2$  production.

With reference to the time period before coal reserves are exhausted, W. Peschka *et al* (Deutsche Forschungs-und Versuchsanstalt ffr Luft-und Raumfahrt, Germany) showed that  $H_2$  can be produced from coal as cheaply as synthetic gasoline or methanol. Thus  $H_2$  may have importance as a low-pollution fuel before the exhaustion of coal reserves. In this same area, Witcofski's report examined production of methane and aviation kerosene from coal. It was found that methane can be derived more cheaply and with better thermal efficiency than kerosene or  $H_2$ , the latter two fuels being comparable in cost and efficiency of derivation. It would appear then that methane may be the short-term energy vector, a point made by J. Pottier (Gaz de France, France) in his survey of the French program in  $H_2$  research.

From this mélange of opinions, the writer concludes that there will be a steady growth in  $H_2$  as an energy carrier through the remainder of this century, but it may play a secondary role to cheaper, more convenient derivatives of coal, some of which are also clean fuels. As coal resources near exhaustion,  $H_2$  should become a major carrier of energy. Further data comparing  $H_2$  with synthetic fuels are given in Section V.

## II. Production of Hydrogen

### A. Fossil Fuel Basis

Virtually all  $H_2$  is produced today from petroleum or coal feedstocks, and several papers described the three processes commonly employed: (1) steam reforming of natural gas and light hydrocarbons, (2) partial oxidation of heavy oils, and (3) gasification of coal. A very thorough paper by H. Teggars *et al* (Rheinische Braunkohlenwerke A.G., Germany) on coal gasification was most appropriate in pointing out that heat from high-temperature nuclear reactors (HTR) can reduce by 50% the amount of coal required. Here the coal would furnish only the carbon in the basic reaction



while the reactor would provide the heat input  $\Delta\text{H}$  as well as heat for carbonization or "coking" of the coal.

### B. Electrolysis

Production of  $\text{H}_2$  by the electrolysis of water, once commonplace but now economically uncompetitive, may again become commercially viable as fossil feedstocks are depleted, while generation of electricity is taken over by nuclear (or other) power stations. A. B. Hart presented the merits of electrolytic production of  $\text{H}_2$  as (1) an ideal application for off-peak nuclear power; (2) suitable for all power plants, not just HTR; and (3) safe and flexible in layout, in that the electrolytic facility can be widely removed from the nuclear reactor. He stated that significant advances should be possible in the efficiency of electrolysis and outlined areas where research is needed.

One route to greater efficiency is through higher temperature. Hart pointed out that the relationship between  $\Delta F$ , the electrical energy required to decompose water, and temperature  $T$  is such that a 30% reduction in electrical power will be realized by increasing the temperature from  $25^\circ\text{C}$  to  $1000^\circ\text{C}$ . (For reference, the functions  $\Delta F(T)$  and  $\Delta Q(T)$ , the electrical work and the heat required for electrolysis of water, respectively, have been plotted in Fig. 1 for temperatures from 300K to 6000K.) Another beneficial effect of increased temperature (and increased pressure as well) is a reduction of voltage losses at the electrode/electrolyte interfaces.

Moving on to ways to achieve higher temperature capability, Hart described two solid electrolytes that may supplant the familiar aqueous alkaline and aqueous acid solutions in electrolytic cells. These are the solid polymer ion-exchange membrane and the high-temperature zirconia film. The polymer membrane, originally developed by the General Electric Corp. for fuel cells, serves as both electrolyte and gas separator. Conduction is via  $\text{H}^+$  ions, and the maximum temperature capability is  $150^\circ\text{C}$ . The zirconia film electrolyte (actually a mixture of  $\text{ZrO}_2$  and  $\text{Y}_2\text{O}_3$ ) can also serve as gas separator. Conduction is via  $\text{O}^{2-}$  ions, and the material can function at  $1000^\circ\text{C}$ . In both the polymer and the zirconia electrolyte, high electrical resistance now limits electrolyte thickness to a few tenths of a millimeter for reasonable performance.

J. C. Sohn *et al* (Université de Grenoble, France) presented power consumption data for France to show that low-load periods of power stations are more seasonal than diurnal in nature. Thus long-term

energy storage (months) is required. The authors consider electrolytic production of  $H_2$  to be the most attractive storage method. They discussed in the paper only the aqueous alkaline electrolytic cell, noting the problems to be encountered in raising the temperature. Evolution of water vapor limits non-pressurized aqueous electrolyzers to about  $80^\circ C$ . Pressurization removes this limit, but corrosion of electrodes becomes increasingly severe above  $100-120^\circ C$ . The asbestos separators long used in aqueous electrolytic cells are limited to about  $110^\circ C$ ; thus the development of better separator materials is a prerequisite for operation at higher temperature. The authors presented data to show that cell power requirements decrease by about 0.4% per degree Centigrade in the range  $80$  to  $160^\circ C$  (Ni electrodes employed).

S. Srinivasan *et al* (Brookhaven National Laboratory) discussed the solid-polymer membrane cell and cited as its chief advantage a maximum current capability five to ten times that of aqueous cells. Disadvantages at present are the high costs of the perfluorinated polymer membrane and of the catalysts (platinum and iridium) with which the surfaces of the membrane are coated. The authors also reported progress on new separators for aqueous alkaline cells and expressed the belief that such cells will soon be operating at  $150^\circ C$ . In regard to zirconia cells, there is work under way in the electrolysis of both water and water vapor. The latter is dictated at the higher temperatures by the high vapor pressure (e.g., 200 atm at  $370^\circ C$ ).

From the papers just discussed, the principal thrust of research in electrolysis appears to be in the development of new materials and construction methods to permit operation at higher temperature. While gains were implied in the papers, quantitative estimates of the effects of higher temperature on cell output and associated heating were not given. Such estimates have been made by the writer, from expressions derived in the Appendix, for the following conditions:

$$\eta = \text{cell efficiency} = 0.6, 0.8$$

$$\text{operating temperature} = 25^\circ C, 1000^\circ C$$

$$\Delta F \text{ and } \Delta H: \quad \text{Fig. 1}$$

The range in cell efficiency  $\eta$  has been taken from Hart's paper and a later one by J. E. Funk *et al* (to be discussed in the next section). Electrical work input will be denoted by E, output in moles of  $H_2$  by N, and auxiliary heating required by H. Results are as follows:

	$\eta = 0.6$		$\eta = 0.8$	
	$\frac{N}{\Delta H}$	$\frac{H}{\Delta H}$	$\frac{N}{\Delta H}$	$\frac{H}{\Delta H}$
25°C	0.75	-0.25E	1.00	0
1000°C	1.00	0	1.33	0.33E

It is clear that the poorer cell ( $\eta = 0.6$ ) benefits substantially from the higher operating temperature. The  $H_2$  output increases by 33% and the requirement to cool the cell, indicated by  $H < 0$  @ 25°C, is eliminated. This cell at 1000°C requires neither heating nor cooling; all heat required by the reaction is furnished by internal dissipation of electrical work. In this condition the cell is said to be "thermoneutral."

The merits of raising the operating temperature of the better cell ( $\eta = 0.8$ ) are more debatable. This cell, thermoneutral at 25°C, produces the same output as does the poorer cell at 1000°C. Raising the temperature of the better cell to 1000°C will increase the output by 33%, but will necessitate injection of heat equivalent to 1/3 the electrical input. This heating of the reactants from an external source implies a substantial increase in cell cost and complexity that may offset the thermodynamic gain from higher temperature.

From the foregoing data at 25°C, it is seen that the efficiency of converting electrical work into chemical energy  $\Delta H$  lies between 0.75 and 1. Now the thermal efficiency of a modern power station is approximately 0.4. Thus the efficiency of converting heat into chemical energy  $\Delta H$  via generation of electricity/electrolysis of water is in the range of 0.3 to 0.4

### C. Thermochemical Decomposition

The future competitor of electrolysis in producing  $H_2$  from water via nuclear (or solar)-generated heat is direct thermochemical (TC) decomposition. As shown in Fig. 1, the electrical work required to separate water into  $H_2$  and  $O_2$  decreases linearly with temperature, reaching zero at 4300K (7281°F). At this temperature no electrical work is required, and heat alone suffices to drive the reaction. Unfortunately, temperatures of this magnitude are almost unattainable, although some work in direct water "splitting" is being done at the French solar furnace installation at Odeillo (ESN 30-7:315).

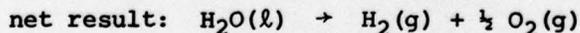
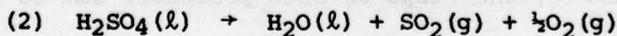
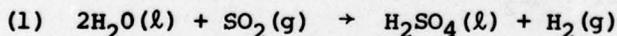
The way around this difficulty is to use a chain of reactions involving one or more elements in addition to  $H_2$  and  $O_2$ , having selected the temperatures required by the individual reactions to be commercially feasible (see Appendix). The auxiliary elements are recovered and reused, so that the net result is simply the separation of water

into H<sub>2</sub> and O<sub>2</sub>. During the past decade the existence of such systems has been established in the laboratory, but a practical industrial process has not yet been demonstrated. Most success has been achieved with "hybrid" systems, where electrical work is used to drive at least one reaction, the remaining reactions proceeding from heat input alone.

TC splitting is one of the most active areas in H<sub>2</sub> technology at present, and several excellent papers in the Conference were devoted to it. B. Estere *et al* (Gaz de France) began with a discussion of the thermodynamics of electrolytic and TC processes. Starting with the primary heat source and working through to the final products H<sub>2</sub> and O<sub>2</sub>, they showed that, under the assumption of reversible sub-processes, both methods for the decomposition of water have the same theoretical efficiency. The similarity arises from the fact that the TC process is in effect a heat engine that absorbs heat at high temperature (endothermic reactions), rejects heat at low temperature (exothermic reactions), and produces net work in the form of chemical free energy. Their conclusion was that the superiority of one process over the other will depend upon the irreversibilities which are introduced in converting the theoretical cycles to engineering practice.

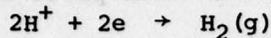
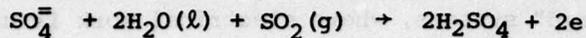
The paper by Esteve *et al* went further in comparing electrolytic and TC processes by including first-order estimates of the various losses that will occur in the two systems. The outcome was that the two processes were again very nearly equal in performance, and even more realistic data would be required to distinguish the better process. These results suggest that a more efficient means for splitting water than electrolysis may not be found. This paper reveals a great deal of careful thought; it should be a good source of ideas and thermodynamic derivations.

J. E. Funk *et al* (University of Kentucky) continued with TC processes by presenting "engineering efficiencies" for some of the more promising chemical systems. These efficiencies are derived by first preparing a flow diagram for the process with all equipment specified, and then employing typical loss data for each piece of equipment to arrive at the final output. The authors first examined the hybrid sulfuric acid cycle, a two-step process pioneered by the Westinghouse Corp.:



The free energy  $\Delta F$  of step 1 is positive and increases with temperature. Thus this reaction is driven electrically in an electrolytic cell at the lowest temperature available (ambient). The

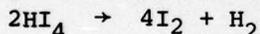
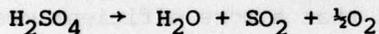
anode and cathode reactions may be expressed, respectively, as



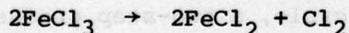
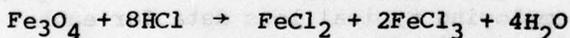
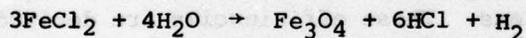
The  $\Delta F$  of step 2 is positive at ambient conditions but decreases with temperature. This reaction is allowed to proceed spontaneously at 1150K. Funk *et al* obtain an efficiency of 0.45 for this TC process; i.e., 45% of the heat put into the process (including that needed to produce the electrical power for step 1) is recovered in the chemical energy of the  $\text{H}_2$  produced. (In the preceding section the corresponding efficiency for the electrolytic method was found to be 30 to 40%.)

Pure TC methods discussed by Funk *et al* were the 3-step iodine-sulfuric acid process and the 4-step iron-chlorine process. Efficiencies of 0.3 to 0.5 were obtained for the former, depending upon the plant layout, and only 0.18 for the latter. The authors believe that the low efficiency of the iron-chlorine process can be improved by optimizing the heat exchange between the process and the basic heat source. The equations for the two processes are as follows:

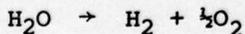
Iodine-Sulfuric Acid Process:



Iron-Chlorine Process:



As may be easily confirmed, the steps of both processes sum to yield



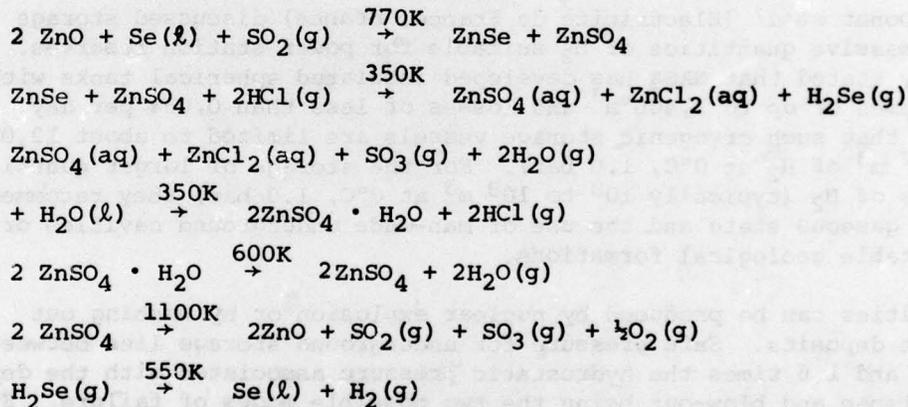
G. De Beni (EURATOM, Ispra, Italy) next reviewed the work in TC cycles conducted at EURATOM, Ispra. Much effort has been spent in trying to improve the iron-chlorine process by, e.g., minimizing the number of heat transfer operations and varying compositions and temperatures. He considers the cycle efficiency still unacceptably low, however. Ispra is now concentrating on the iodine-sulfuric acid cycle and

two hybrid sulfuric acid cycles. One of the latter is the Westinghouse process. The other is a variant in which the electrolysis of  $\text{SO}_2$  is replaced by a reaction between  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{Br}_2$ , followed by electrolysis of  $\text{HBr}$  to release  $\text{H}_2$ . De Beni, and others as well, noted the widespread use of computers in conducting systematic searches for promising TC cycles.

The last presentation on TC processes for splitting water was a critical review by M. G. Bowman (Los Alamos Scientific Laboratory) of all cycles under study in the U.S. His first point was that much effort has been wasted in considering theoretically attractive cycles without first experimentally demonstrating that all reactions involved will proceed at useful rates. Accordingly, his paper dealt only with cycles of the "small and select group" where such experimental verification exists. These are listed as follows, with notation as to the originator, the number of steps in the process, and the maximum temperature required:

Argonne National Lab.; 4 steps; 900K  
 Lawrence Livermore Lab.; 6 steps; 1100K  
 Oak Ridge National Lab.; 3 steps; 1000K  
 General Atomic Co.; iodine-sulfuric acid cycle; maximum temperature not stated  
 Westinghouse Corp.; hybrid sulfuric acid cycle; 1150K

For purposes of illustration, the set of equations for the Lawrence Livermore Lab process is listed as follows:



Despite the success with hybrid cycles, Bowman urged that research in pure TC cycles continue, saying, ". . .it seems too early in the search to abandon the potential advantages of the pure cycles. . ." Looking toward the future and possible availability of solar energy, he called attention to a promising cycle recently proposed by the Institute of Gas Technology. A hybrid based upon the electrically driven reaction of Cd with water to release  $\text{H}_2$ , followed by thermal decomposition of  $\text{Cd}(\text{OH})_2$  to recover the Cd, the cycle requires a maximum temperature of 1500K (2240°F). To achieve this temperature, concentrated solar energy was recommended. (The French group

at Odeillo is working with a pure TC, 2-step process involving ZnO at 2200K (see previous ESN reference and Appendix.)

From these papers it appears that the contest between the classic process of electrolysis and the promising newcomer, TC splitting, is going to be very close. The fundamental thermodynamics as presented by Esteve *et al* predicts this, and the experimental results to date tend to support this conclusion. The hybrid sulfuric acid cycle does appear to be somewhat better "on paper" than electrolysis, but it still has not been implemented in an operating plant; also, it is not a pure TC process. The principal advantage of TC splitting, namely, production of  $H_2$  from heat without the intermediate step of generating electricity, is strongly offset by the complexity of the chemical operations and the cumulative effect of losses incurred in the multi-step decomposition process.

### III. Storage of Hydrogen

If  $H_2$  is to attain the status of energy vector that its proponents foresee, much progress is required in techniques of storage. On the one hand it will be necessary to store enormous quantities of  $H_2$  from off-peak power station production, the period of accumulation being measured in months. On the other hand,  $H_2$ -powered vehicles will require light and compact storage of quantities sufficient for reasonable cruising ranges.

#### A. Underground Storage

G. Donat *et al* (Electricité de France, France) discussed storage of massive quantities of  $H_2$  suitable for power station reserves. They stated that NASA has developed insulated spherical tanks with volumes of up to  $3,400 \text{ m}^3$  and losses of less than 0.05% per day, but that such cryogenic storage vessels are limited to about  $12,000 \text{ m}^3$  ( $10^7 \text{ m}^3$  of  $H_2$  at  $0^\circ\text{C}$ , 1.0 bar). For the storage of larger quantities of  $H_2$  (typically  $10^8$  to  $10^9 \text{ m}^3$  at  $0^\circ\text{C}$ , 1.0 bar) they recommend the gaseous state and the use of man-made underground cavities or suitable geological formations.

Cavities can be produced by nuclear explosion or by washing out salt deposits. Safe pressure for underground storage lies between 0.6 and 1.6 times the hydrostatic pressure associated with the depth, collapse and blow-out being the two possible modes of failure. Storage sites of this type for natural gas exist in several countries. Use of the technique for  $H_2$  should present no difficulties, although for reasons related to differences in thermodynamic properties, storage of  $H_2$  is expected to be two to four times more costly per unit of energy than storage of natural gas.

A paper by W. Van Deelen (TNO - Special studies group, The Netherlands) on the energy scenario for The Netherlands envisioned storage of  $H_2$  in the by-then-depleted natural gas fields. Donat *et al* had noted

one problem in this regard: contamination of the  $H_2$  by hydrocarbons remaining in the field.

### B. Metal Hydrides

A promising method for storing  $H_2$  is to form a metallic compound that can be readily decomposed to recover the  $H_2$  fuel. The first paper on the topic was by R. Schmitt (Battelle, Switzerland), who pointed out the disadvantages of storage in pressure vessels and in cryogenic form. In terms of energy density the best pressure vessels give only 1.0-1.7 kWh/kg. Cryogenic storage provides 33 kWh/kg (ignoring weight of tank and insulation), but 14 kWh/kg  $H_2$  must be expended to liquefy the gas. Schmitt felt that evaporation losses (0.5% to 1.0% per day quoted) would rule out this system for private motor vehicles, although not for vehicles in continuous use.

Hydride storage offers the potential advantage of an energy density appreciably better than that of pressure vessels without the associated high  $H_2$  pressures. Schmitt presented thermodynamic data for 10 promising hydrides. Energy densities ranged from 0.3 to over 4.0 kWh/kg (LiH:4.2,  $MgH_2$ :2.5,  $CaH_2$ :1.6). The more efficient reactions tend to have high equilibrium temperatures and high dissociation enthalpies  $\Delta H$  ( $CaH_2$ :920°C, 24.2 kWh/kg $H_2$ ; LiH:800°C, 25.2;  $MgH_2$ :280°C, 10.3). The user, of course, must provide this operating temperature and the heat input  $\Delta H$  to extract the  $H_2$  from the hydride. As noted by Schmitt, however, the requirement for appreciable  $\Delta H$  is not really a problem; the heat engine which burns the fuel discards most of the  $H_2$ 's 33 kWh/kg heat content anyway, and this heat can be used as input to the hydride unit.

Schmitt continued with a discussion of the various hydrides in regard to kinetics, stability, pressure-temperature-concentration characteristics and, finally, cost. For both stationary and mobile storage, the hydride  $FeTiH_2$  was considered the best choice for first-generation applications. This hydride, while not a high-energy type, decomposes at ambient temperature with modest heat input (energy density: 0.3 kWh/kg, equilibrium temperature: -10°C,  $\Delta H$ : 4 kWh/kg  $H_2$ ). Because of the low energy density, installation of a  $FeTiH_2$  unit would be feasible only in a large vehicle such as a bus. For second-generation applications, Schmitt believed  $MgH_2$  has the most promise. The weight of the storage unit would be reduced by an order of magnitude, but provisions for maintaining 300°C and increased heat input would be required.

C. Gales *et al* (Centre d'Etudes Nucléaires, France) continued with the topic of hydride storage by reviewing what they consider to be the three most promising compounds:  $LaNi_5H_6$  (also listed by Schmitt),  $MgH_2$ , and  $FeTiH_2$ . The first, while low in energy density (0.45 kWh/kg), is very dense, comparing favorably with liquid  $H_2$  in energy/volume. Another merit is its low equilibrium temperature: 40°C at 2-atm pressure.

The authors consider  $MgH_2$  to be the best hydride from the energy-density point of view, and much effort has been devoted to applying it to storage systems for automobiles. In the course of charge-discharge tests on  $MgH_2$ , the group discovered a severe aging problem: a 75% loss of capacity after only six cycles. This has been corrected by adding Cu to form  $Mg_2CuH_2$ , and the required heat input  $\Delta H$  has been reduced at the same time.

The hydride  $FeTiH_2$  was only briefly discussed in the paper. It is considered promising for stationary storage of  $H_2$  but unsuitable for mobile applications because of low energy density.

### C. Cryogenic Storage

Techniques for storing  $H_2$  in liquid form have been highly developed in conjunction with the space program. The only paper of the Conference devoted solely to this form of storage was that by W. Peschka *et al* (Deutsche Forschungs-und Versuchsanstalt für Luft-und Raumfahrt, Germany). The frequently heard objection that the power required to liquefy the  $H_2$  makes the concept uneconomical was answered in the paper with the statement that waste heat from any method of  $H_2$  production (TC splitting, electrolysis, or coal gasification) is sufficient to furnish the shaft power to liquefy the gas (efficiency of heat to shaft power conversion of 0.3 assumed). In view of the facts that (1) practical processes for TC splitting have not been defined and (2) the process of generating electricity and electrolyzing water produces waste heat only at near-ambient temperature where the energy is unavailable for further work, it would appear that this statement requires qualification.

Some preliminary analytical comparisons of liquid  $H_2$  with gasoline for automobile fuel showed that the  $H_2$  provides about the same cruising range per unit mass of storage system as the gasoline, and two to three times more than a hydride system. A solution to the problem of loss through boiling was suggested in the form of a small Mg-hydride unit to absorb the  $H_2$  boiled away. The authors believe that such a system in a typical automobile would prevent loss of  $H_2$  for periods of up to 10 days.

The authors discussed also the possibility of storing  $H_2$  by adsorbing it at low temperature (typically 77K) on substances such as activated carbon and nickel silicate. They stated that storage densities comparable to that of liquid  $H_2$  are possible, although the maximum value apparent in the data presented was 0.14 gm  $H_2$  per gm adsorbent.

### D. Remarks

A comparison will be made of the various media available for mobile energy storage. Energy densities for liquid  $H_2$  and metal hydrides are listed below, together with those of gasoline and certain types of batteries (ESN, 30-11:497).

<u>Storage System</u>	<u>Energy Density (kWh/kg)</u>
liquid H <sub>2</sub>	33
hydrides	0.3 to 4.0
gasoline	13
batteries	
lead-acid	0.02
Ni-Fe	0.05
Na-S	0.20

The energy densities of the various storage media are seen to differ by about three orders of magnitude. The disparities are reduced somewhat by consideration of typical efficiencies for converting stored energy to shaft power:

heat engine: 25%  
 fuel cell plus electric motor: 40%  
 electric motor: 75%

The first two conversion methods are applicable to H<sub>2</sub> (liquid or in hydride) and gasoline; the third to batteries only.

#### IV. Future Uses of Hydrogen

Today, when the feasibility of producing H<sub>2</sub> as a fuel has not been established, many researchers consider it premature to work on future applications. This was succinctly expressed at the Conference by H. Marchandise (Commission des Communautés Européennes, Belgium) in a policy statement that ". . .it is necessary to be able to produce H<sub>2</sub> economically before devoting too much effort to using it." Nevertheless, there were informative presentations on a number of possible applications, and certain of these will be reviewed.

##### A. Recovery of Coal

J. Ribesse (Distrigaz, Belgium) presented a paper on *in situ* recovery of coal from strata inaccessible to normal mining methods. The procedure consists of injecting gases into the coal vein via pipes, producing a reaction with the coal, and withdrawing reaction products of significant energy content. The quality of gas produced depends upon the gas injected. Hot air produces a poor product (970 kcal/m<sup>3</sup> @ 35 atm) that is not marketable and must be utilized in a power station at the site. Oxygen gives a better result (2400 kcal/m<sup>3</sup>), but H<sub>2</sub> is excellent (9500 kcal/m<sup>3</sup>) in that the coal is converted into methane:



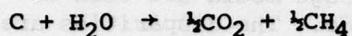
Field experiments to date with the injection technique have involved only air, but work with H<sub>2</sub> is beginning in several countries.

Ribesse expects an efficiency of 58% in converting energy of coal into energy of methane delivered by the plant.

It is important to note that, in this process, all the H<sub>2</sub> injected into the earth is generated at the site through the reaction



Thus, half the methane produced from the coal is consumed in making H<sub>2</sub>. Summing the two preceding equations yields the net reaction:



It is seen that this process is not a future use of nuclear-generated H<sub>2</sub>, but a way to convert inaccessible coal deposits into high-quality fuel with H<sub>2</sub> a component of the process. Given the relative abundance of coal resources, the environmental and economic problems in recovering them, and the necessity to convert coal into a more compact and clean fuel, this *in situ* recovery work seems of highest priority.

#### B. Fuel for Internal Combustion Engines

C. Gales *et al* (Centre d'Etudes Nucléaires, France) described experiments in converting three conventional power plants to H<sub>2</sub>-fuel: a single-cylinder, 2-hp gasoline engine, a 4-cylinder Renault gasoline automobile engine, and a 250-hp gas turbine. The two gasoline engines were modified only by adding a gas carburetor and changing the valve timing. In both cases, the power delivered with H<sub>2</sub> was approximately the same as with gasoline. Efficiency was unaffected as well, account being taken of the difference in heats of combustion between gasoline and H<sub>2</sub>. Preliminary results for the gas turbine were described as "very satisfactory."

Internal combustion engines fueled by H<sub>2</sub> were also discussed by Y. Breele (Institut Francais du Pétrole, France). On the basis of tests conducted by others and not referenced, he observed that, in converting from gasoline to H<sub>2</sub>, efficiency is unchanged, but power is reduced about 25% (12% in theory) because of the lower energy content per unit volume for a stoichiometric mixture of H<sub>2</sub>. Pollution is substantially reduced; emissions consist primarily of oxides of nitrogen and traces of hydrocarbons from oxidation of lubricants.

Breele's preference, however, for H<sub>2</sub> utilization in vehicles is the fuel cell/electric motor combination. Efficiency is about twice that of an internal combustion engine. He distinguished three types of cell, which corresponded to the alkaline, acid, and high-temperature ceramic electrolytic cells discussed earlier by Hart. (We are now reversing the electrolysis process.) The alkaline cell is considered by Breele to be the best for vehicle application, and performance data for 1980 were taken as follows: energy

conversion efficiency--50%, power density--125 W/kg and 65 W/dm<sup>3</sup>, and life--3,000 hours of operation. It was concluded that a vehicle competitive in speed, range, and price with a diesel-powered automobile can be built, although matters such as safety and cell life under adverse operating conditions remain to be explored.

### C. Aircraft Fuel

R. D. Witcofski (NASA, Langley Research Center) presented results of a lengthy series of studies of H<sub>2</sub>-powered aircraft. Here the problem is one of storing sufficient fuel without compromising aircraft performance and utility. Volume and weight limitations dictate that liquid H<sub>2</sub> must be used. NASA has found that aircraft designed to carry this fuel are generally comparable in energy consumption with those using conventional jet fuel, and slightly better at the longer ranges. Techniques for handling liquid H<sub>2</sub> have been developed in the space program, and they are considered compatible with fueling practices in large commercial and military aircraft. No problems in fueling or turn-around time are foreseen. The most serious technology gap is in the insulation requirements of the aircraft fuel tanks. Existing insulation materials are too brittle to resist thermal strains and too porous to stop gases in the air from passing through and condensing on the tanks.

### V. Efficiencies of Fuel Production

We return now to the topic of the future role of H<sub>2</sub> *vis-à-vis* that of fuels derived from fossil sources, especially from coal. Estimates of fuel production efficiencies have been taken from various Conference papers and listed below. The quantity presented is thermal efficiency, defined to be the ratio of heating value of the fuel produced to the quantity of heat required to produce it, including the heat needed to generate any electricity used in the process. (Numbers in parentheses denote references listed below the table.) In the case of H<sub>2</sub> production from water, the thermal efficiency is the product of the thermal efficiency of producing gaseous H<sub>2</sub> (taken to be 0.35 from earlier discussion) and the efficiency of converting gaseous to liquid H<sub>2</sub> (taken from the papers referenced). All fuels are assumed to be in the liquid state.

<u>Fuel Produced</u>	<u>Raw Material</u>	
	<u>Coal</u>	<u>Water</u>
methane	0.69(1)	-
aviation kerosene	0.55(1)	-
hydrogen	0.56(1), 0.43-0.48(2)	0.21(3), 0.25(1)
methanol	0.43(2)	-
gasoline	0.41(2)	-

- (1) R. D. Witcofski (NASA Langley Research Center)  
 (2) W. Peschka *et al* (Deutsche Forschungs-und Versuchanstalt für Luft-und Raumfahrt, Germany)  
 (3) R. Schmitt (Battelle, Switzerland)

The following observations are made:

1. Only coal can yield hydrocarbon fuels (there is no carbon in water!).
2. Of the hydrocarbons, methane is the most efficiently produced. The efficiencies for H<sub>2</sub> and the remaining hydrocarbons are approximately the same.
3. The efficiency of producing H<sub>2</sub> from water is about half that of producing it from coal.

These calculations show a clear advantage for synthetic hydrocarbon fuels. The efficiency of producing H<sub>2</sub> from water compares unfavorably with all the other data, and H<sub>2</sub> produced from coal offers no advantage over the liquid hydrocarbons, which necessitate little modification of existing machines. If cryogenic storage and gaseous fuel can be accommodated, then methane--not H<sub>2</sub>-- would seem the reasonable choice.

It is important, however, to note that these estimates take no account of energy expended (and other costs) in mining and transporting the coal to the conversion site, or in reclaiming mined areas. When these factors are considered, H<sub>2</sub> produced from water may compare much more favorably with coal-based fuels.

APPENDIXI. Heat and Work in Chemical Reactions

The fundamental equation governing heat and work in chemical reactions at constant temperature  $T$  and pressure  $P$  is

$$\Delta H = \Delta F + \Delta Q \quad \dots (1)$$

where  $\Delta F$  = free energy change

$-\Delta F$  = work (e.g., electrical work) that the reaction can produce reversibly at constant  $P$  and  $T$  (work due to volume change excluded)

$\Delta H$  = enthalpy change

$-\Delta H$  = heat released if the reaction occurs irreversibly at constant  $P$  and  $T$

$\Delta Q$  = heat that must be added to keep  $T$  constant during the reversible reaction

=  $T \Delta s$ , where  $\Delta s$  is the entropy change

All quantities in equation (1) are functions of  $T$ , and two must be determined experimentally to characterize fully the reaction. As an example, data for the decomposition of water are given in Fig. 1. We see that  $\Delta H$  is nearly independent of  $T$  and is positive; i.e., enthalpy is increased by the reaction. The free-energy change  $\Delta F$ , the electrical work required to electrolyze water, is positive at low temperatures but decreases almost linearly with  $T$  and passes through zero at 4300K.  $\Delta Q$ , the heat that must be added to maintain temperature, increases as  $\Delta F$  decreases. At 4300K, no electrical work is required, and the reaction will proceed from heat alone. Above this temperature,  $\Delta F$  is negative; the reaction will actually furnish electrical work while absorbing heat. The discontinuities in the functions  $\Delta F$  and  $\Delta Q$  are produced by the change in state of water at 373K and 1 atm. The  $\Delta F$  relation in Fig. 1 has been calculated from data on the equilibrium constant  $K(T)$  via the relationship

$$\Delta F = -RT \ln K$$

The function  $\Delta F(T)$  depends upon the concentration of reactants and products. The curve in Fig. 1 pertains to the case where the  $H_2O$ ,  $H_2$ , and  $O_2$  gases participating in the reaction are at 1-atm partial pressure. By changing pressures it is possible to shift the  $\Delta F$  curve. If the partial pressures of the  $H_2$  and  $O_2$  are reduced to  $\frac{1}{2}$  atm, for example, the dashed curve in Fig. 1 is obtained.

II. Electrolysis

Expressions will be derived for the  $H_2$  production and the net heat requirement of an electrolytic cell. It is assumed that the heat recovered on cooling the electrolysis products to ambient temperature is just sufficient to raise the incoming water (or water vapor) to process temperature. We define the following terms:

$E$  = electrical work input  
 $N$  = number of moles of  $H_2O$  electrolyzed, or moles of  $H_2$  produced  
 $\eta$  = efficiency, or  $N \Delta F / E$   
 $D$  = electrical work dissipated as heat, or  $E - N \Delta F$   
 $\Delta H' = \begin{cases} \Delta H & \text{for } T < 373K \\ \Delta H + 10.55 \text{ kcal/mole} & \text{for } T > 373K \end{cases}$   
 $H$  = heat required in addition to  $D$ , or  $N(\Delta H' - \Delta F) - D$   
 $a = \Delta F / \Delta H'$  at temperature  $T$  from Fig. 1

The quantity added to  $\Delta H$  for  $T > 373K$  is the heat required to change the incoming water to water vapor. Thus  $\Delta H'$  is a continuous function of  $T$  (no discontinuity at 373K).

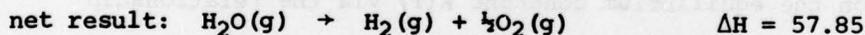
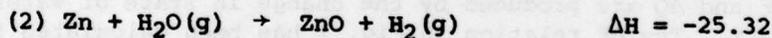
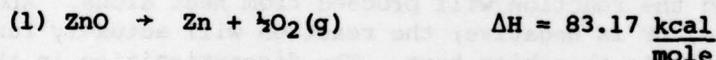
The desired quantities are

$$N = \eta \frac{E}{\Delta F} = \frac{\eta}{a} \frac{E}{\Delta H'}$$

$$H = N(\Delta H' - \Delta F) - E + N \Delta F = E \left( \frac{\eta}{a} - 1 \right)$$

### III. Multi-Step Decomposition of Water

As shown in Fig. 1, decomposition of water by heat alone is possible only for  $T > 4300K$ . However, as first described by Funk and Reinstrom (I & EC Process Design and Development, 5, 336 (1966)), lower temperatures will suffice if a properly chosen series of reactions is employed. This is illustrated with the following 2-step process:



The sum of the free energy functions for the two component reactions must be precisely the function for the net reaction, curve 3 in Fig. 2. Yet if the two component free-energy changes are of opposite sign at low temperature, the individual curves can cross zero at temperatures well below 4300K. This is illustrated in Fig. 2 for reactions 1 and 2 preceding. Reaction 1 is endothermic, and its free energy change crosses zero at 2200K. Above this temperature, then, this reaction will proceed spontaneously (heat input to maintain temperature being assumed). Reaction 2 is exothermic, and it will proceed spontaneously for  $T < 1400K$ . Thus this 2-step process should effect the decomposition of water with maximum temperature in the neighborhood of 2200K.

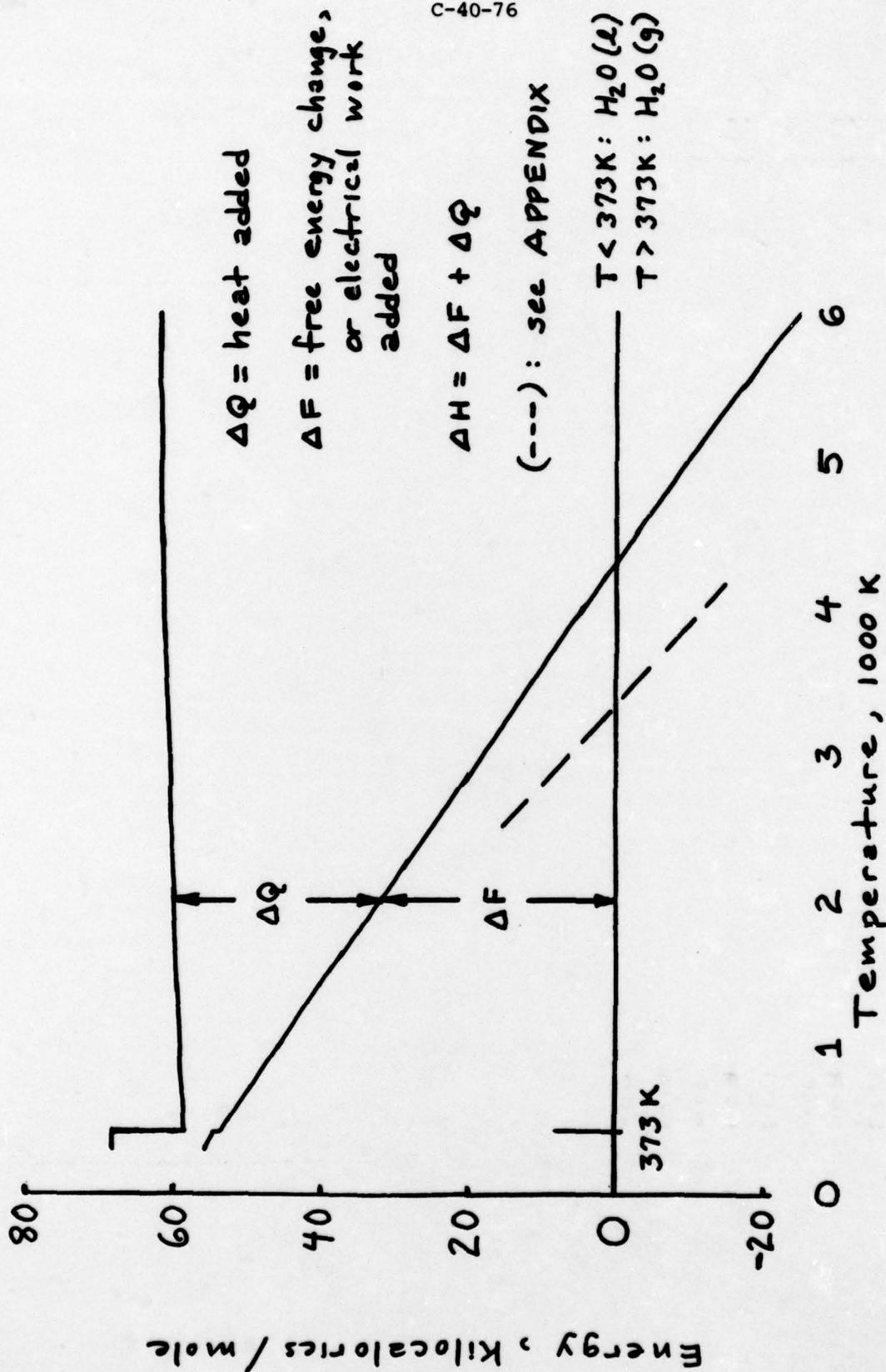


Fig.1 Thermodynamic Functions for  $\text{H}_2\text{O}(l \text{ or } g) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$   
 All gases are in standard state - 1 atm partial pressure  
 Reference: Nat. Bureau Stds., NFRDS - NBS 37, June 1971

- (1)  $ZnO \rightarrow Zn + \frac{1}{2} O_2$  j)
- (2)  $Zn + H_2O(g) \rightarrow ZnO + H_2(g)$
- (3)  $H_2O(g) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$

(Curves 1 & 2 are approximate only.)

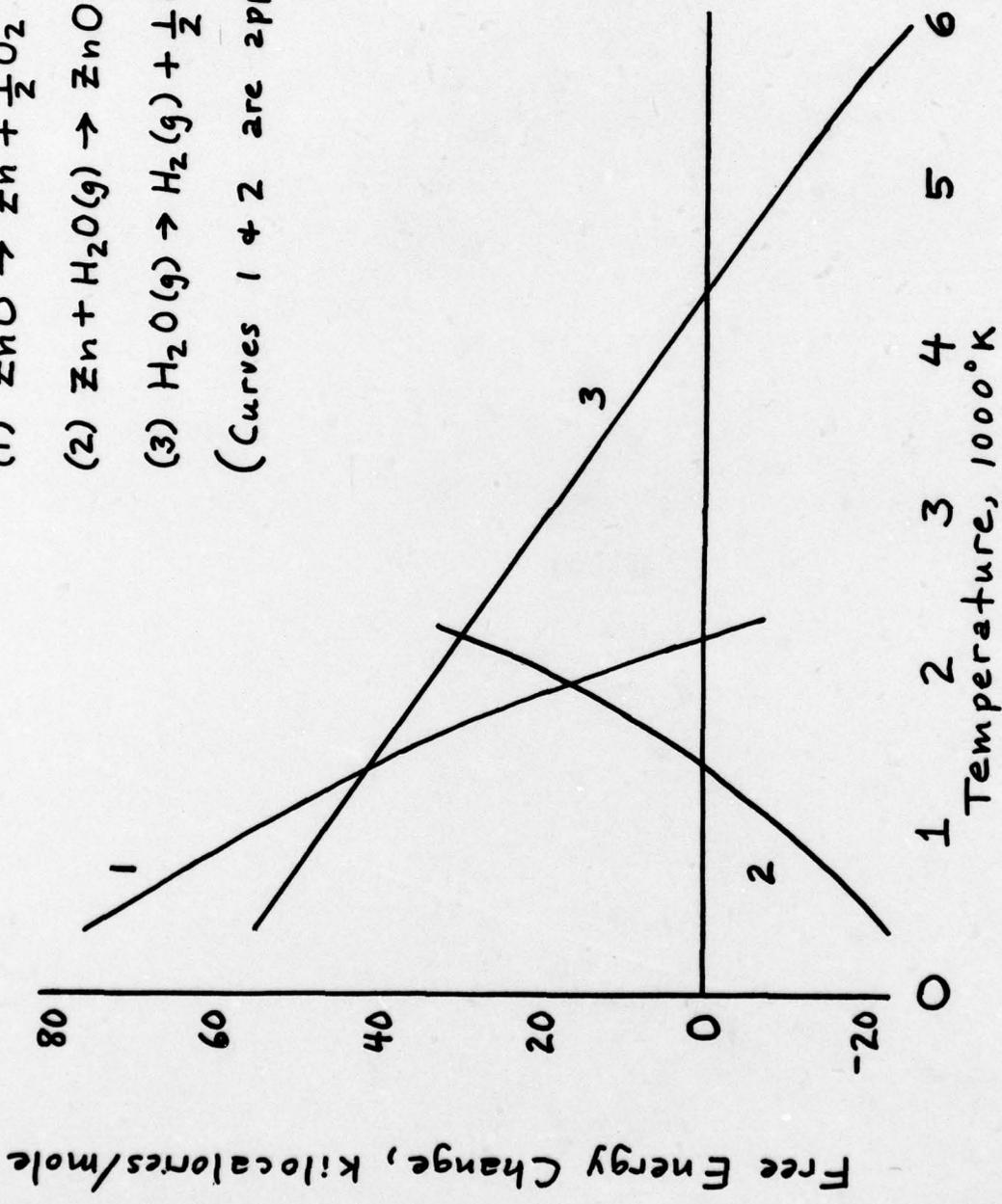


Fig. 2 Free Energy Functions for Three Reactions

(References for ZnO data: Handbook of Chemistry & Physics, 46<sup>th</sup> ed., p. D-49)  
 ESN 31 July 1976, p. 315

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