

# CHEMICAL CYCLE PROCESSES FOR IMPROVEMENT IN CONVERSION AND RATIONAL USE OF ENERGY

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Received: April 15, 1982  
Presented by Dr. Gy. CSOM

## Summary

The substitution of increasingly depleting fossil fuels for a diversity of unconventional energy sources with a new and improved power generation is an urgent task of science and technology. Chemical cycle processes involved in the energy conversion mechanism, such as the two step reversible dissociation of dinitrogen tetroxide, may potentially improve the conversion efficiency. Hydrogen producing chemical cycles are designed to supply chemical energy into the Hydrogen Energy System and to bridge over therewith the periodical availability of new energy options with good storage and distribution feasibility. These chemical cycles have new thermodynamic burdens, but they may provide a better overall efficiency of direct heat and radiation energy conversion to stored chemical energy in comparison with those of conventional methods. To develop the Hydrogen Energy System is the common interest of both the energy and chemical industries.

Keywords: chemical energy; chemical cycle processes; cycle thermodynamics; energy conversion efficiency; hydrogen energy; nitrogen tetroxide; nuclear energy; nuclear breeder; solar energy.

## Energy resources

Energy is the basic natural resource, its availability is the question of primary importance in the prosperity, economical and population growth of modern society. The world-wide concern over the present energy shortage relates to the depletion and apparent exhaustion of fossil fuel sources, one of the smallest, but widely used options of power generation. Moreover, along with OPEC manipulation, the energy and chemical industries are the competitors on the market of these raw materials. At the same time, we are ample in other forms of energy resources, which have not sufficiently penetrated to the energy industry so far for various reasons. Renewable energy sources, such as wind, wave, tidal, geothermal and water powers are of local, regional and/or seasonal availability, therefore they cannot cope with the flexibility of chemical energy sources. Although the economically recoverable part of these renewable sources can cover only a small part of world's energy needs, except of some

occasional chemical pollution of geothermal sources, they are important, environmentally clean, energy sources in specific regions.

The most abundant energy source is the solar radiation which, in principle, could be tapped to cover all presumable energy requirement of human civilization without inflicting any considerable damage to the biosphere by such human activity. However, the solar energy received by the earth's surface is intermittent, disperse by area and wavelength distribution, and diffuse in space, therefore, its harvest needs unconventionally large and expensive equipment, its efficient conversion is also limited by wave length threshold and quantum yield, and its daily and seasonal cycle must be bridged over with energy storage means of large capacity for continuous use. Actually, the solar energy has all the properties inconvenient entropically to be collected and converted into a usefully concentrated energy form. Therefore, a high efficiency of conversion cannot be expected, not even the biological systems were able to develop a path of photosynthesis better than 4% efficiency during their seasonal periods of vigorous biological activity. The man-made converters are of better efficiency ranging from 12% of photovoltaic conversion up to the theoretical 30% efficiency of photochemical conversion applying the solar spectrum of high threshold energy (900—1200 nm wavelength). Such devices have found application of small scale energy output, e.g. for house heating, but it is still open to debate whether a sun-powered plant of high output with land based collectors would economically be feasible in the future to supply energy to a large scale industrial complex.

Nuclear energy is a virtually inexhaustible source if the breeding of abundant  $^{238}\text{U}$  to  $^{239}\text{Pu}$  and  $^{232}\text{Th}$  to  $^{233}\text{U}$  is taken into account. The prospective fusion power offers even a larger source of energy next to solar energy source, especially the  $\text{D} + \text{D}$  thermonuclear reaction, however, it requires unpredictably hard conditions of plasma confinement, whereas the  $\text{D} + \text{T}$  reaction, under intensive research at present, is somewhat limited by the long range supply of  $^6\text{Li}$  isotope used for tritium breeding.

To be industrially effective, an energy source must be compact. Nuclear energy can easily be concentrated, the power plant operates with steady output without the short term problem of refueling and is practically uninfluenced by external factors. Hence the nuclear power plant is the most reliable electricity supplier to a large industrial complex, but, it is less convenient to supply other sectors as it cannot follow the periodical peak demands. The general use of present thermal neutron converters are in need of a more sophisticated fuel cycle, including an acceptable nuclear waste management, and some improvement in operational safety and heat conversion efficiency. In comparison, fast breeder reactors produce less nuclear and heat waste per unit output of electricity, mainly because of their higher thermal efficiency, and, by

having a strong negative Doppler coefficient of reactivity, they are not exposed to core melt down accident of fatal consequences.

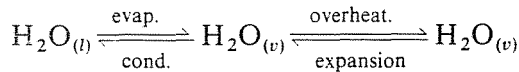
The main problem with energy is not its world-wide shortage, but rather that natural gas and oil are rapidly depleting and will have to be replaced. Probably, the world will run out of some vital material resources earlier than of energy itself. Each variety of replacement has its own technical scope of development, however, the economy-related constituents are much subjected to debate, namely, which options, or what combination of existing ones are better suited for a new long-range energy system. On narrow bases it might lead to an emotional choice. Recently, the WELMM concept, an acronym taking into account the five scarce resources — Water, Energy, Land, Materials and Manpower — seems to favour polyenergetic systems with various mixes of primary energy [1]. Anyway, the price of new substituting provisions will be higher fuel costs, therefore, it is evident that energy, as our primary commodity, should be used more efficiently with care of conservation. Energy conservation, beyond being the central feature of energy policy, so far has been successfully carried out on the user's side, but what can be done technically on the producer's side?

The reply of that question requires a throughout thermodynamic analysis of predominantly applied heat-to-work conversion processes both of conventional fluid-vapour physical cycles and recent chemically active conversion cycles. Special interest should be devoted to those complex chemically active cycles where the sequence of conversion steps can be interrupted at the stage of energy accumulation deposited in a concentrated chemical form, which then can be well stored and easily distributed to local users. This distinct quality of chemical energy provides a new concept for the rational use of energy. Consequently, the purpose of the present paper is to give a comprehensive survey of thermodynamics of practicable novel energy conversion cycle processes with special concern to their thermodynamic or thermochemical restrictions of efficiency. In the following papers to be published later on, each type of feasible or prospective cycle options of energy conversion will be evaluated separately with special interest to find out their thermodynamic burdens, and to analyse the possibilities how to overcome the thermodynamically restricting steps with cycle hybridization applying a combined heat and radiation input to the conversion system.

### **Energy conversion and storage**

A given energy source needs to be converted into a useful form of power, such as electricity or mechanical motion. Thermal type power stations are converting the heat content released from fossil or nuclear fuels into

mechanical energy in the turbine expansion process either of the closed Rankine-cycle operated with a working fluid-vapour medium, or of the closed Brayton-cycle operated with a working gas. The conversion of the turbine mechanical energy to electricity is performed with 98—99% efficiency of the electric generator (the highest efficiency of all known energy conversions), but the thermal to mechanical conversion is restricted by the second law of thermodynamics. Water is predominantly used as a working fluid, its change of state having performed during the four-step cycle may be represented by the following simple formula:



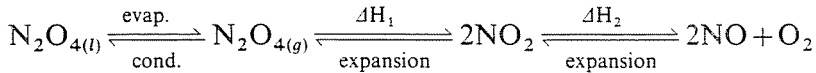
where subscripts (*l*) and (*v*) stand for liquid and vapour states. This is the best known thermal cycle with no mole number change therein (the chemical potential change of the system is zero), thus the principle of hydrodynamic similarity can be well applied to the system without any complication for modelling and optimizing the cycle. Combining the first and second laws of thermodynamics, the maximum thermodynamic efficiency of such ideal cycle is

$$\frac{W}{Q} = 1 - \frac{T_c}{T_t}$$

where *W* is the work performed by the system, *Q* is the heat input, *T<sub>c</sub>* and *T<sub>t</sub>* are the top and cooling temperatures of the cycle, respectively. Applying this equation to a most efficient power station of *T<sub>t</sub>* = 840 °K and *T<sub>c</sub>* = 310 °K, the maximum thermodynamic efficiency is 63% assuming an ideal Carnot cycle and complete reversibility, but, discounting all irreversibilities of a well designed Rankine steam cycle including the boiler efficiency and the power ratio used for sustaining the cycle, the actual efficiency drops to about 35%. The heat content of complementary efficiency is dissipating as waste heat. With the shares of energy spent on mining and preparation of burned fuel deduced including the loss on the electric grid system, no more than 25% of the original heat input will be delivered to the user in the form of electricity. It may appear to be dissatisfactory, but that is the case when thermodynamics is involved.

The annexed Fig. 1 shows the effect of temperature on the theoretical thermal efficiency and the actual efficiency of real conversion cycles, assuming that the working medium is cooled to 300 °K at the cycle closing section. By increasing the top temperature higher efficiencies can be achieved through the use of a combination of the characteristic conversion technique with steam cycle as a topping stage. However, the increase of top temperature requires expensive construction materials and the risk of a system break-down is also increasing.

The demonstrated conversion techniques are fairly developed, therefore, any further improvement may rather be expected in the use of residual thermal energy by lowering the heat rejection temperature (to be entailed with a bottom cycle). So far no practical thermal conversion technique has been able to exceed the 56% barrier of efficiency. The best approach of the theoretical efficiency is developed in the top temperature range of 550—850 °K. However, the breakthrough in thermal efficiency seems to be attainable through using a chemically active working fluid, such as dissociating dinitrogen tetroxide ( $N_2O_4$ ), at lower top temperature. Such a six-step Gokhstein working cycle [2] can be represented by the following formula:



where subscript (*g*) stands for the gaseous state,  $\Delta H_1 = 57.39$  kJ/mole and  $\Delta H_2 = 113.24$  kJ/mole are the heats of first and second step chemical dissociations. The first step dissociation is not as well separated from the liquid phase [3] as shown by the above simplified formula, but it can be shifted to the gas phase by increasing the pressure of the heat take-up section of the cycle. At 170 bars the degree of dissociation ( $\alpha_1$ ) at the starting section is about 1%. Under such pressure the first step dissociation is completed at 550 °K, just the temperature at which the second step dissociation starts. The top temperature

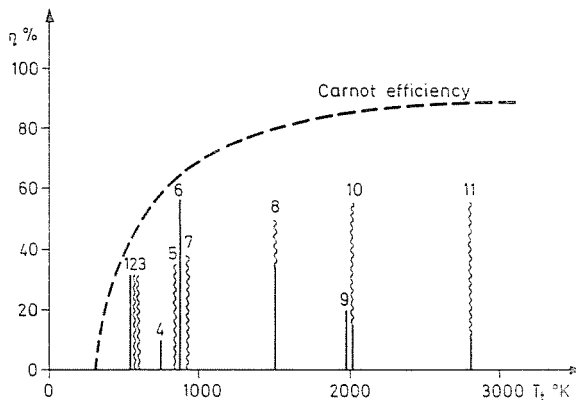


Fig. 1. Efficiency and operating top temperature of various thermal energy conversion systems: 1.  $N_2O_4$  with  $\alpha_1$  degree of dissociation, 2. BWR, 3. PWR, 4. Thermoelectrics (based on the Seebeck effect), 5. Conventional steam turbine cycle, 6.  $N_2O_4$  with  $\alpha_1 + 0.33 \alpha_2$  degree of dissociation, 7. AGR, 8. Gas turbine with steam topping stage, 9. Thermionics (with cesium plasma), 10. MHD closed cycle and 11. MHD open cycle, both with steam topping stage. ——— characteristic efficiency, ~~~ steam turbine as characteristic or topping stage efficiency

of the cycle can be set to 850 °K, over which the irreversible chemical decomposition of  $\text{NO}_2$  would exceed 1% per year. At such top temperature and pressure conditions the degree of the second step dissociation ( $\alpha_2$ ) reaches 35%.

In consequence of the two reversible chemical dissociations, the mole number is changing throughout the cycle, thereby its thermodynamic efficiency can theoretically be increased by the maximum amount of work obtainable from the Gibbs potentials ( $\Delta G_1$  and  $\Delta G_2$ ) of reversible reactions:

$$100 \frac{\Delta G_1}{\Delta H_1} + 35 \frac{\Delta G_2}{\Delta H_1} = 23.5\%$$

provided that the hydrodynamics of the cycle could be well synchronized with the relaxation times ( $\tau$ ) of reversible chemical processes. It can be implemented in the case of the first step dissociation, the relaxation time of which is  $\tau_1 \sim 10^{-8}$  s under the above conditions, while  $\tau_2 \sim 10^{-3}$  s and it raises some technical difficulties to be exploited completely as mechanical work, but its heat content can be recycled with intermediate regeneration. Due to the enthalpy differences of the chemical reactions, the values of both the specific heat of the working fluid and the heat transfer are very high (22—50 kJ/kg and about  $10^7$  kJ/m<sup>2</sup> · hour [4]), thereby a high heat flux can be realized in the cycle at relatively moderate temperature as needed in nuclear reactors. In the  $\text{N}_2\text{O}_4$  condensing cycle the turbine outlet volume is about 35 times smaller than that of steam power plants, therefore, the turbines and other auxiliary equipment of the cycle are much smaller than those of steam cycles of the same capacity.

Up to now the  $\text{N}_2\text{O}_4$  dissociating cycle has been designed as secondary circuit to the CANDU-PHW [5] to take advantage of thermodynamic properties of  $\text{N}_2\text{O}_4$  turbine and condensing sections. But  $\text{N}_2\text{O}_4$  has also favourable nuclear physical and radiation properties, therefore, it may effectively be used as gas coolant of fast neutron reactors for maintaining a high breeding ratio of plutonium. As the enthalpy differences of the chemical dissociations constitute 50—55% of the overall heat take-up, 900—1200 kW per litre thermal load can be achieved in the reactor space. Both factors contribute to the resultant short doubling time of the nuclear fuel breeding.

According to the design of direct  $\text{N}_2\text{O}_4$  cycle nuclear power station of 1000 MW capacity with a fast breeder reactor operating at 550 °K top temperature, 29% of thermal conversion efficiency can be reached [4], however, the 850 °K top temperature variant with relatively high ratio of heat regeneration and intermediate superheating carried out at optimized pressure of heat bleed may attain 56% of thermal efficiency [6]. Since the doubling time ( $t_2$ ) of plutonium is approximately inversely proportional to both the power density (P, kW/kg) of the fuel and the breeding coefficient (KB),

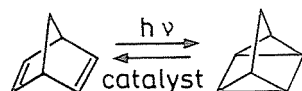
$$t_2 \sim \ln 2 / P(\text{KB} - 1)$$

by increasing the top temperature of the cycle from 550 to 850 °K, both the power density and KB will decrease due to lower heat flux and negative nuclear reactivity feedback, thus extending the doubling time from about 5 years up to 10 years, estimated on the basis of 1 year external fuel cycle. In principle, this connection suggest that such type of power station with top temperature regulation would be capable of taking up nearly 100% of peak load fluctuation in the electric grid system at the temporary expense of plutonium breeding. Such inherent compensation of thermal conversion with the nuclear performance of the reactor has not yet been elaborated theoretically.

Along with high thermodynamic and breeding indices, the  $N_2O_4$  system has some disadvantages, such as its corrosiveness, especially at gas-liquid phase boundaries, and the toxicity of  $NO_x$  compounds. Nevertheless, the  $N_2O_4$  system exhibits a prominent example how the cycle performance can be improved by the chemical potential change.

The human activity consumes various energy forms, mainly released from fossil fuels which are generally accused of air and environmental pollution. Electricity, sharing about one fifth of the overall energy consumption, is the convenient clean form of energy, but it has the burden of transport and storage. Electrical transmission is the most expensive method of energy transportation with considerable loss on the transmission line, while the efficiency of hydroelectric storage, the only feasible method today, is about 65%, and the sites for such storage are limited. Therefore, the operation of electric industry has to meet the vagarious variations in demand with standby electrical capacity for generation and transmission. The situation is not better for thermal or mechanical energy storage.

Apart from electrochemical means, heat storage in chemical accumulation is a promising option. Photochemical pericyclic reactions of reversible bond rearrangement, such as photoisomerization, photoadduct formation and photodimerization [7], provide feasible systems for heat storage along with chemical conversion of solar energy. The photoisomerization of norbornadiene to quadricyclane is one of the most attractive solar energy storage



reactions where the enthalpy of isomerization is 1110 kJ/mole. The starting compound absorbs the solar radiation with the wavelength threshold of 300 nm to form the prismane derivative, then the stored energy can be recovered later as heat by pumping the photoproduct past an immobilised catalyst of transition metal complexes. The efficiency of this heat recovery is 36% due to the heat loss in cascading of excited electrons from the higher vibrational levels and in relaxation from the transition state of norbornadiene.

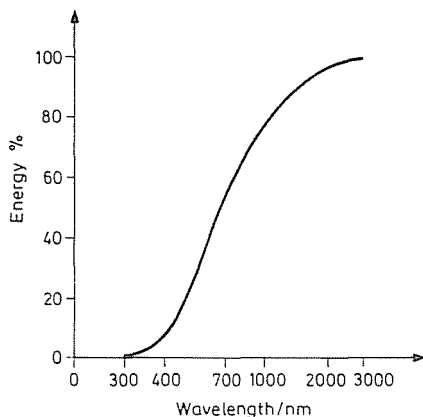


Fig. 2. Energy distribution of the solar spectrum received by the earth surface

Nevertheless, this system is capable of storing four times more heat comparing with a conventional solar water heating system, the low wavelength threshold of absorption deprives of its acceptable overall efficiency.

Figure 2 shows the spectral distribution of solar energy received by the earth surface on clear mid-summer days at around forty degrees of north latitude [8]. The curve points to the importance of the wavelength threshold value in the overall efficiency of photochemical processes driven by solar radiation. Recently, the spectral absorption range of norbornadiene has been extended to the visible region by photocatalysis of monovalent copper complexes [9], but with lower quantum yield.

The photochemical solar heat conversion and storage system provide low value heat of 100—150 °C top temperature, since their application is limited to house-heating. Photodegradation, irreversible polymerization and other side reactions may cause some loss of the medium, the products of which accumulate on repeated cycling.

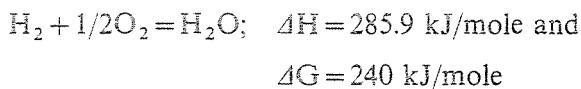
### Hydrogen energy system

All the above inadequacies of storage and distribution could be eliminated by the prospective implementation of the Hydrogen Energy System (HES), according to which the energy obtained from various sources is applied to produce hydrogen as secondary energy carrier of excess negative entropy content by using direct thermochemical or radiation processes for water splitting. Hydrogen is an ideal carbon free fuel for avoiding the global CO<sub>2</sub> impact. It can be well stored under pressure or in the form of metal hydrides, it is easy to distribute through pipelines, so it can be used on the spot by



converting into thermal, mechanical and electric energy — according to necessity — with high efficiency. Moreover, hydrogen is an important feedstock for chemical and metallurgical industries, and at this point they should be the potential cooperators to develop the methods of large scale cheap hydrogen production.

The heat content of hydrogen per unit weight is about three times greater than that of graded hydrocarbon fuels, but, even in the liquid form, hydrogen requires four times the volume of its heat equivalent in gasoline. Hydrogen could be supplied for residential and commercial use in pipelines as used to be the case with town gas earlier in this century, or it can be blended with natural gas up to 15% by volume and burned directly without modification of existing combustion equipment or distribution lines. It can also be burned in internal combustion (IC) engines with minimal redesign which in turn, will improve the efficiency at partial load and increase the maximum power output of IC engines. The only polluting  $\text{NO}_x$  formation can be well controlled by water injection which also reduces the backfiring in the intake manifold. If the distribution of hydrogen for automotive traction, or the hydrogen storage aboard vehicles should prove technically difficult, there is still the option to convert it into ammonia and to use as  $\text{NH}_3$  fuel directly, or with interposed ammonia decomposer. But the most efficient use of hydrogen is its direct conversion to electricity in fuel cells. The efficiency of electrochemical power sources is not restricted by the thermodynamic limitation of the heat engine, hence the hydrogen cell is capable of operating with efficiency between 60—80% depending on the rate of power production. As the chemical process of cell conversion is



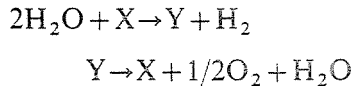
it is the most advanced process to approach the maximum amount of work obtainable from the reaction ( $\Delta G/\Delta H=0.84$ ). To be competitive with the thermal power generation, the efficiency of hydrogen production should attain 45—60%. Above that threshold value all other advantages of the HES will netly proceed.

### Large scale hydrogen production

Steam reforming of hydrocarbons and coal gasification reactions produce hydrogen with 70% and 60% conversion, respectively, but those conventional processes are consuming the dwindling reserves of fossil fuels, and the obtained product has to be separated and purified to meet the requirements of most hydrogen users. Electrolysis, the advanced solid polymer

electrolyte variant, which can be performed with 32% efficiency of overall energy conversion, would be paradoxical, except for using off-peak electricity for hydrogen fuel generation. Therefore, rather the unconventional methods of hydrogen production, such as thermochemical, radiolytic and photochemical water splitting, are subjected to intensive research recently.

Water, the abundant raw material for hydrogen production, is a compound of high chemical stability, its  $\Delta G$  value vanishes at about 4400 °K temperature and the input heat energy dissociates the water molecule into free atoms of high energy content. Therefore, the amount of primary energy to split water is one of the highest among common chemical reactions, and the high temperature of thermolysis would impose extreme technological conditions for such single step decomposition. When it is carried out at lower temperatures, the thermochemical water splitting, which can be taken for direct heat-to-chemical energy conversion, is carried out in a closed cycle process consisting of several consecutive reaction steps (usually from 3 to 6 ones) with heat and water input and outlet of hydrogen, oxygen and degraded heat, where the process heat is usually taken from a nuclear converter of a very high temperature reactor (VHTR) with an outlet temperature of about 1250 °K. As the overall thermal efficiency of the cycle depends on the conversion product of consecutive chemical reactions, it is a general trend to compose the cycle of the possible minimum number of chemical steps, however, at least two consecutive steps would have the advantage of evolving hydrogen and oxygen separately, such as



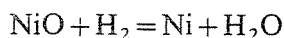
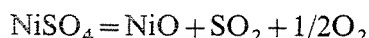
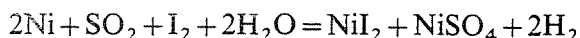
A large number of thermochemical cycle processes has been proposed, investigated and tested on bench-scale experiments. The most extensively studied processes belong to three main categories having similar elements or reactions, these are:

1. The sulfur process, wherein  $\text{X} = \text{SO}_2$  and  $\text{Y} = \text{H}_2\text{SO}_4$ ;
2. Bromine or iodine promoted sulfur processes, wherein  $\text{X} = \text{SO}_2 + \text{Br}_2$  or  $\text{I}_2$  and the formation of  $\text{H}_2$  is carried out in a separate reaction step of hydrogen halogenide dissociation,  $\text{Y} = \text{H}_2\text{SO}_4$ ;
3. Metal halide processes, where the best known representatives of  $\text{X}$  are  $\text{FeCl}_2$ ,  $\text{CaBr}_2$  and  $\text{MgI}_2$ , resulting either in higher oxide form of  $\text{Y}$ , such as  $\text{Fe}_3\text{O}_4$ , along with  $\text{HCl}$  and direct  $\text{H}_2$  formation, or in the corresponding oxide (or hydroxide) and hydrogen halogenide of  $\text{X}$ , then followed by reaction steps of hydrogen halogenide dissociation and reconverting  $\text{Y}$  to  $\text{X}$ .

The variation of thermochemical cycles within the above categories are aimed at lowering the reaction temperature and avoiding to handle highly corrosive solutions. For the same reason, they are occasionally hybridized with

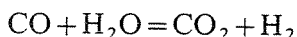
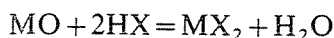
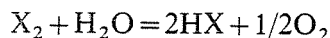
electrolytic, radiolytic, photolytic or catalytic processes, increasing therewith the degree of freedom of the system.

The theoretical efficiency of pure thermochemical cycles may come close to 60% [10], but the actual thermal efficiency is around 30% at the present level of development. With multi-step heat regeneration it can be increased to 35—40%, and with hybridization to 45—50% approximately. As a prominent example, the NIS (Nickel—Iodine—Sulfur) cycle [11] of JAERI (Japan Atomic Energy Research Institute) might deserve special attention. It is an improved variant of category 2 consisting of four basic steps:



which may be divided into more sub-steps according to the necessity of chemical technology. This cycle is specially designed for VHTR heat source with four heat bleeds of different temperature to “gear” the power output of the reactor in synchrony with the rate of chemical reactions. Secondary steam and nitrogen lines are serving to attain 0.76 heat recovery ratio, thus resulting in 35% thermal efficiency of the cycle, which is quite acceptable when hydrogen is produced for chemical purposes. The detractive section of the cycle is the cycle-closing fourth step, wherein half of the produced hydrogen is consumed for nickel oxide reduction. However, in case of NiO, carbon monoxide has much better reducing capacity than H<sub>2</sub> below 1000 °K of reaction temperature. Therefore, if the NiO reduction could be combined with a secondary CO<sub>2</sub>/CO thermochemical cycle of at least 30% thermal efficiency, the NIS cycle would approach the most desired 60% value of the overall thermal efficiency under the original reaction conditions of the NIS system.

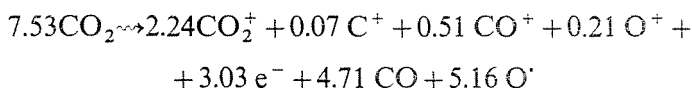
Another class of hydrogen producing thermochemical cycles, which may also be designed for process-heat utilization of VHTR, is based on the reduction of CO<sub>2</sub> to CO in the reaction of metal halides (MX<sub>2</sub>) or carbonates, such as MnCl<sub>2</sub> and FeCl<sub>2</sub> (or carbonates), CrCl<sub>3</sub>, CoCl<sub>2</sub> and NiCl<sub>2</sub>, with CO<sub>2</sub>, then hydrogen is produced by the water shift reaction [12]:



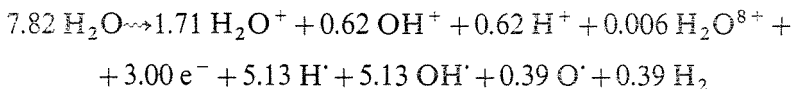
These cycle processes have some advantage of being less corrosive in the chemical technology by avoiding the hydrolysis of metal halides, however, separation procedures of gaseous intermediate and final products are rather inconvenient. The relatively low rate of CO formation, as well as the side reaction branching in the 2nd and 3rd steps at elevated temperature have dropped the initial interest in research. The CO<sub>2</sub>/CO thermochemical cycles are not as thoroughly investigated as the direct water splitting cycles, nevertheless, they might draw interest in special cases of metallurgy, such as the above NiO reduction.

Both water and carbon dioxide molecules have very stable chemical structure, hence they are used as moderators and heat carriers in nuclear reactors. However, using nuclear radiation sources which are emitting ionizing particles of high linear energy transfer capacity, they undergo radiolytic decomposition resulting in H<sub>2</sub> and CO product, respectively. Regarding primary radiation sources, plutonium fission (3.5 MeV neutrons), but expediently D + T fusion (14.1 MeV neutrons) are the most prospective ones [13]. Such processes can be taken for direct conversion of radiation into chemical energy. By leaving off the intermediate stage of thermal conversion, and with the primary act of radiolysis not limited by thermal equilibrium, we may expect a higher energy conversion efficiency theoretically.

The primary stage of carbon dioxide radiolysis [14] caused by the direct absorption of 100 eV energy of radiation:



where the enthalpy change of this reaction is 916 kJ/mole (71.5 eV calculated for 100 eV energy absorbed). The energy difference is spent for subexcitations of electrons and excitation processes of ions and radicals. Similarly, the primary stage of water radiolysis [15]:



where the enthalpy change of the reaction is 869.1 kJ/mole (70.4 eV calculated for 100 eV energy absorbed). However, these two reactions have a semi-quantitative correspondence between the yields of primary intermediate species, there is a difference of prime importance, that is the hydrogen formation occurs with much lower G value (molecules of product CO or H<sub>2</sub> per 100 eV radiation energy absorbed) than the carbon monoxide formation even in the initial stage.

In both cases of CO<sub>2</sub> and H<sub>2</sub>O, the primary act of radiolysis occurs with high efficiency of somewhat more than 70% energy take-up [15] mainly in the

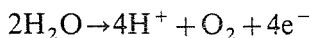
form of chemical energy deposit, but the primary energy change, consisting of ionization and bond cleavage, is followed by a series of charge-transfer clustering reactions, charge elimination and radical (and/or free atom) termination reactions. Since all the subsequent processes are exothermic chemical reactions and not all of them lead to the desired CO or H<sub>2</sub> formation, moreover, some of them are typical back reactions, the G-value of the process becomes slightly temperature dependent. Due to the dissipation of reaction heat and the product consuming back reactions, the efficiency of primary energy conversion is sharply reduced even if the back reactions are chemically inhibited to some degree. In that case of CO<sub>2</sub> radiolysis, G(CO) varies between 4.5 and 10 which corresponds to 13 and 30% energy conversion efficiency, respectively. Water radiolysis comprises a more complex chemical mechanism, which conflicts with chemical inhibition of back reactions. At the present state of development, the radiolysis of liquid water is capable of producing H<sub>2</sub> with approximately 3% efficiency of radiation energy conversion.

The hydrogen production through CO<sub>2</sub> radiolysis followed by CO shift reaction and CO<sub>2</sub> recirculation seems to be more promising than the direct radiolysis of water. Unless the back reactions of charge elimination occurring in the track of fission fragments are suppressed, the direct radiation conversion to chemical energy could not afford the expected high efficiency. Chemical purity is also a formidable requirement in radiolysis. The separation and purification of gaseous products formed in the CO<sub>2</sub> splitting cycle is an awkward task of chemical technology. For such reason, radiolysis is rather used as a suitable hybridizing step of thermochemical water splitting cycles, like e.g. promoting the dissociation step of hydrogen halogenide [13].

Along with thermal and photovoltaic conversion of solar energy, there is a great effort in research to develop competitive photochemical processes for hydrogen production by water splitting, thereby connecting the solar energy source into the HES directly. The immediate use of solar heat for hydrogen production by water thermolysis in sun furnace of ~3500 °K temperature proved to be unrealizable because of the reactor material and H<sub>2</sub>/O<sub>2</sub> separation technique problems.

Photochemical processes are already widely used for chemical synthesis, where to obtain an acceptable high yield, reaction mechanisms involving a chain propagation step are preferred enabling therewith to use the photons of the light source with ~10<sup>3</sup> quantum yield, like in the case of photochlorination of alkanes. Although, photosynthesis with quantum yield of unity is also used on large scale, like the photonitrosation of cyclohexane to produce cyclohexanone oxime, an intermediate in caprolactam production developed by Toray Industries in Japan. But, even in these processes of relatively low photoactivation energy requirement, the photon energies of solar radiation are too low and UV sources are employed in practice. The photodissociation of water

is, however, a more complex problem, as the products of four single electron transfer steps are needed in an accumulated form to generate one molecule of oxygen:



then followed by hydrogen producing charge elimination reaction. Although four protons of the near infrared band would have sufficient energy to photolyse two water molecules, there is no reaction mechanism by which such a four electron transfer can take place in one step. Since the HO—H bond energy is 495 kJ/einstein, which corresponds to the threshold energy of photons of 186 nm wavelength, the water molecule can be broken up by using far UV radiation which leads to high energy species of H<sup>•</sup> and HO<sup>•</sup> radicals and ions. Such short wavelength band takes about 0.1% fraction of the extraterrestrial solar spectrum, and the quantum yield of this reaction is about 0.33.

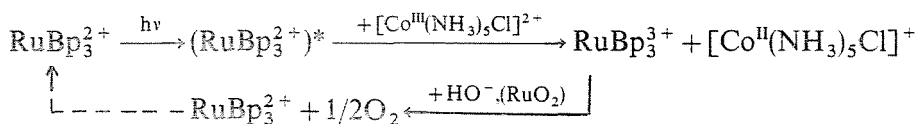
To carry out such multi-step reaction with excited and charged species, the charges have to be separated and accumulated in the first step for further use in a channelled charge elimination. According to the present state of art, it can be done either by using membranes in which the light absorber and the splitter are embedded, and which represent some kinetic barrier to prevent immediate electron transfer in the reverse direction, or the primary step of reaction is carried out on the surface of an electrode photoexcited by light irradiation to the potential adequate for electrochemical decomposition of water, and this electrode siphones the charges toward the desired charge elimination. Both variants lead to the construction of a photochemical cell in which recombination is prevented by the removal of electrons into an external circuit.

Another attempt is to enlarge the band gap of useful wavelength which can be achieved by sensitization. Sensitisers are apparently able to promote the retention of absorbed energy long enough to enable more than one photon to take part in the process. With all these complications the photochemical water splitting process is a combination of sensitized photo-excitation and electrolytic redox steps.

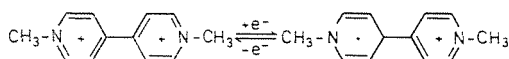
Among devices for photosensitized electrolytic oxidation of water on solid surfaces, the best known cell construction is the n-type semiconductor TiO<sub>2</sub> electrode [16] immersed in diluted NaOH solution and photoexcited to negative potential required for O<sub>2</sub> evolution by being irradiated with light of 415 nm threshold wavelength, which corresponds to the band gap of TiO<sub>2</sub>. The counter electrode is made of platinum and immersed in diluted H<sub>2</sub>SO<sub>4</sub> solution where the cathodic process of charge elimination occurs accompanied with H<sub>2</sub> evolution. The quantum efficiency of this process is 0.1 approximately at monochromatic irradiation. Several other n-type semiconductor electrodes [17] as irradiated anodes and p-type semiconductor electrodes as irradiated

cathodes have been investigated to enlarge the band gap of absorbed light, to shift the hydrogen evolution reaction toward more positive potential, and to find more stable electrodes resistant against oxidizing degradation of electron-hole pairs at the anode side.

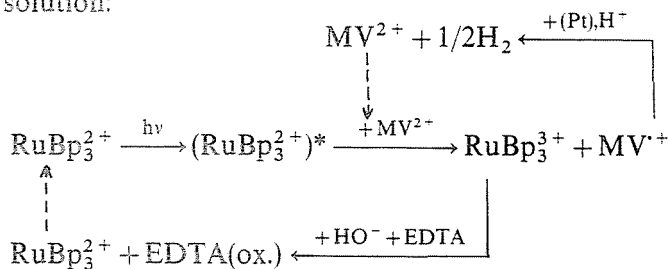
There are effective sensitizers among organic dyes and azo-complexes of metals. The action of water soluble ruthenium bipyridinium-chlorate,  $\text{RuBp}_3^{2+}$  (Bp = 2,2'-bipyridinium), has a high extinction coefficient and wide overlap with UV-visible spectrum up to about 700 nm wavelength which covers 50% range of extraterrestrial solar energy distribution (see Fig. 2). If the excited electron is irreversibly transferred to reduce  $\text{Co(III)/Co(II)}$  complex [18], the ground state ion of high redox potential is capable of oxidizing water when using ruthenium dioxide catalyst partially embedded in polyvinyl alcohol dispersion:



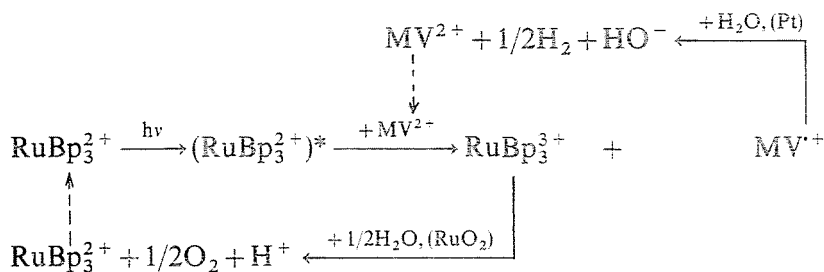
Aromatic amines, nitroaromatics and dipyridinium ions are reversible electrontransferring complexes with high quenching rate [19]. Methylviologen,  $\text{MV}^{2+}$  (1,1'-dimethyl-4,4'-bipyridinium dication) removes the excited electron of the ruthenium sensitizer:



then, the radical cation formed can be reoxidized upon reducing water and promoting the hydrogen evolution on catalysis with either platinum fine particles also embedded partially in hydrophobic polyvinyl alcohol dispersion, or hydrogenase enzyme [20], while the  $\text{RuBp}_3^{3+}$  complex is reconverted by the irreversible oxidation of EDTA or ascorbate to prevent oxygen evolution in the bulk of the solution:



The implementation of the combined photochemical disperse system for complete splitting of water with colloidal catalysts of ruthenium dioxide and platinum:



is of low efficiency and unstable as the processes on the colloidal catalyst particles, which serve for microelectrodes of low overvoltage, have to compete with rapid back reactions. Such practical system has to be divided by membrane for separate oxygen and hydrogen generations. Recently, a biophotolytic system [21] has been reported consisting of chloroplast sensitizer immobilized in flat film form in alginate gel reinforced on nylon grids and stainless steel, of ferredoxin or methylviologen as electron carriers and of hydrogenase enzymes or platinum-polyvinyl alcohol colloid dispersion as catalysts. In spite of its modest efficiency, this rigid matrix synthetic system seems to be the break-through toward large scale solar converter for hydrogen production from water.

The conversion efficiencies of all the above water splitting solar converters are varying from 2 to 15% at present, not exceeding those of solid photovoltaic and photogalvanic systems, which convert solar energy to electricity directly. Although the solar converters are not restricted by thermal equilibrium in the usual sense, extreme high conversion cannot be anticipated because the lower excited states of both the splitting molecules and sensitizers will reverse with heat dissipation in complete accordance with the second law of thermodynamics. Since the field of this technology is still in its infancy, the efficiency is not the primary concern of research, but rather to construct reliable systems of acceptable service life (the longevity of existing devices ranges from a few minutes to about one day), as the constituents are usually very sensitive to free oxygen concentration, and to find out how to govern the rate ratios of consecutive chemical reactions to suppress the back reactions.

Photochemical fuel generation is a rapidly developing area of science, where new results may be expected every day. This new option will not abolish the large land requirement for harvesting sun power, but it would facilitate to join the solar energy into the general HES. There is also a prospective chance to exploit the solar radiation for hybridizing some existing thermochemical water splitting cycles, like in the case of Mark 5 and 6 cycles [22], where the photochemical reaction is applied to carry out the redox process between  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{I}_3^-*/\text{I}^-$  taking advantage of the relatively high molar absorption coefficient of  $\text{I}_3^-$ .



## Conclusions

The main advantage of the HES is the great flexibility of hydrogen as fuel to all requirements of energy use, conversion, storage and distribution, and there is no competitive candidate even with respect of environmental pollution. It brings all the varieties of energy options concluded by WELMM [1] to a common denominator which offers the generalization of the future energy system. Because of the high investment spent already for the existing energy systems, no quick change-over to the HES can be anticipated, but rather a slow evolution, during which those solutions fitting best to the present system will be preferred. However, the chemical industry may be an exception. No doubt it would benefit first from large scale and cheap hydrogen producing technologies.

The efficiency of energy conversion is not the main issue of constructing an energy system, there are the forms of energy source availability and many other diverse economic, environmental and local factors to be taken into account. But the efficiency provides a plausible basis for the comparative thermodynamic analysis of different conversion techniques. Introduction of reversible chemical cycle processes into the energy conversion mechanism might enable us to approach or, in special cases, circumvent the thermal barrier of conventional energy conversions, but new burdens are encountered. The core of the problem is how the free energy content, which is increased by the chemical potential of the system, can be converted into work or stored chemical energy along a cycle conversion [23]. Apparently, such cycles have not enough degree of freedom to select the most efficient path for each step. It is especially valid when the task is to convert optional energy forms into chemical energy either directly or through a chain of conversions. Ironically, its reverse conversion is the oldest manipulation of mankind with energy. The research activity in this field improves the efficiency of power generation and opens new ways to change the pattern of energy utilization, and it will also supply chemical feedstock on large scale for the chemical industry.

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