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## ISOTOPE EFFECTS IN: a) CATALYTIC GENERATION OF HYDROGEN FROM SODIUM TETRAHYDRIDOBORATE AND b) OXYDATION OF HYDROGEN IN FUEL CELLS

*We have investigated deuterium/hydrogen (D/H) isotope effects a) during catalytic evolution of hydrogen gas from the water solution of sodium tetrahydridoborate (NaBH<sub>4</sub>), the sodium borohydride fueled hydrogen generator HGen-E, Fractal Carbon, with the carbon monolith supported platinum reactor was used; b) oxidation of hydrogen in a PEM-type fuel cell to produce electrical energy. We used the E-TEK membrane electrode assemblies with an active area of 4 cm<sup>2</sup>, assembled in a two fuel cell stack.*

*Both processes are important as possible parts of an energy-hydrogen-energy cycle. Any transfer of energy into hydrogen or vice versa induces a change of the D/H isotope ratio, which can be considered from the isotope separation point of view and possible development of a method to produce heavy water as a by-product of the above cycle. In this way, the separation efficiency can contribute to the overall efficiency of the cycle. This work is an initiative to take the isotope effects into account while cycling energy via some specific processes.*

*We measured the isotope separation factor ( $\alpha$ ) of the single-stage process, as a basic parameter determining the isotope separation efficiency.*

*The results proved that deuterium migrated to the dense (liquid) phase in both systems. Average values of the obtained separation factors are:  $\alpha_{(a)} = 5.4$   $\alpha_{(b)} > 12$ . The results obtained could serve for a model for optimization purposes rather than to improve the separation efficiency of a particular unit. To do that it would primarily be necessary to play with a variety of catalysts, which was beyond the main aim of this work.*

*Key words: hydrogen energy, sodium tetrahydridoborate, fuel cell, isotope separation.*

The idea of using hydrogen as an energy medium appeared more than a hundred years ago. It is now considered very seriously for several well know reasons: Hydrogen can be produced from inexhaustible resources by using different primary energy sources, such as nuclear, solar, wind or fossil. It can be easily converted into either heat (by combustion), to supply conventional internal combustion machines, or directly to electricity in fuel cells, with efficiency highly above that of classical thermal machines. In all cases there are almost no negative environmental effects, since water is the only by-product. Finally, it is very suitable for the energy storage and transport.

There are three natural hydrogen isotopes on the Earth: (i) Light hydrogen (*protium*) – <sup>1</sup>H with an abundance of 99.985%, which is predominant and most common one; (ii) Deuterium – <sup>2</sup>H (D) having an average abundance of 0.015%. It can be produced by a number of methods, like electrolysis, chemical exchange, distillation, etc. Main uses of deuterium are as neutron moderator in nuclear fission reactors of PHWR type (in the form of heavy water), and possibly as a fuel component in fusion thermonuclear reactors of the future; (iii) Tritium – <sup>3</sup>H (T) is a radioactive hydrogen isotope with an abundance of T:H = 1:10<sup>18</sup>, (one T atom

per 1 cm<sup>3</sup> of air, or total T amount on Earth – 3.5 kg). Uses: Fuel component in fusion thermonuclear reactors along with D.

Due to their unique properties, all three hydrogen isotopes are of great importance for human activities, especially for energy production, now or in the future. Under the name *natural hydrogen* (or simply *hydrogen*) we always understand a mixture of these three isotopes. It is now produced in huge quantities all over the world, mostly from natural gas. Worldwide industrial production of hydrogen gas is 30 million tones per year. It is consumed for quite different purposes, but still half of the production is used for the synthesis of ammonia. However, it has great potential as a medium suitable for efficient manipulation with energy.

The main purpose of this work was to investigate fundamental isotope effects and isotope separation potentials of two opposite "hydrogen transferring" processes: a) When hydrogen gas is evolved from the water solution of *sodium tetrahydridoborate* (NaBH<sub>4</sub>) using a special catalyst. This process is commonly characterized by the rate of hydrogen evolution for the given catalytic reactor and the NaBH<sub>4</sub> concentration at a temperature; b) When the hydrogen gas is "burned" in the presence of oxygen in the PEM (Proton Exchange Membrane) type hydrogen fuel cell (FC), giving water as the product. This process is commonly characterized by the energy (voltage and current at the fuel cell) released per mass unit of hydrogen consumed under defined conditions.

Why are the isotope effects important? Because when such an aspect is taken into account while cycling

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energy within an *energy–hydrogen–energy cycle*, which is true basis of the hydrogen energy concept, it might help reducing overall expenses of that cycling. Namely, any transfer of primary energy into hydrogen and vice versa is accompanied with changes of the D/H isotope ratio in compounds involved. By a careful consideration of this fact it can be used to extract deuterium as a by-product from cycling hydrogen.

We investigated the isotope effects in regard to the D/H ratio. However, the results obtained can easily be applied to the T/H or T/D ones, taking into account corresponding relations between them, depending on their atomic masses, and very well known from the theory of isotope effects.

Efficiencies of the separation units are independent on their energy efficiencies. We were not focused on the latter here, although we have taken some data in this view. Anyhow, they must be simultaneously considered in attempts to optimize the overall efficiency.

Strong recent development of the fuel cell systems offers an extra possibility regarding the aim. Using them to convert the energy stored in hydrogen directly to electricity rather than to burn it, can additionally improve the concept.

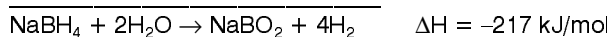
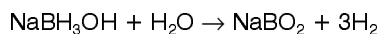
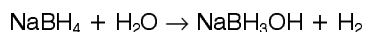
It should be noted that an FC could also be based on the sodium tetrahydridoborate solution as a fuel, where the total isotope effect is a complex function of the separate effects studied in this work. This also might be an interesting theme for future isotope investigations.

Additionally, the hydrogen isotope effects studies in either catalytic hydrogen generators of proton conductors, are of another special interest because they may provide essential information on the state and kinetics of reactions.

There are not too much literature data on the isotope issue of the above systems. An interesting theoretical consideration was recently performed by Tsidilkovski [1].

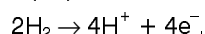
### Description of processes

a) The sodium tetrahydridoborate ( $\text{NaBH}_4$ ) reacts with water to form hydrogen and sodium metaborate ( $\text{NaBO}_2$ ) according to the following mechanism

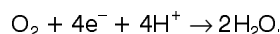


This reaction does not normally proceed spontaneously, and solution of  $\text{NaBH}_4$  in water is quite stable. Some form of a catalyst is usually required. Conventionally accepted catalysts are metal halides, carbon-supported platinum, Raney nickel, noble metals on metal oxides and resin supported ruthenium [2–4].

b) In fuel cells hydrogen fuel is being oxidized producing water, heat and electrical energy. At the anode hydrogen ionises, realising electrons and creating proton ( $\text{H}^+$ )



At the cathode, oxygen reacts with electrons taken from the electrode, and  $\text{H}^+$  ions from the electrolyte, to form water.



In a hydrogen-fed fuel cell, water is produced at the rate of one mole for two electrons [2]. Thus, the rate of water production can be calculated from the following equation

$$\begin{aligned} \text{The rate of water production} &= \\ &= 9.38 \cdot 10^{-8} \cdot \frac{P_e}{V_c} \text{ kg s}^{-1} \end{aligned} \quad (1)$$

where  $P_e$  is electrical power and  $V_c$  is voltage of the cell.

### EXPERIMENTAL

Separation of isotopes from a binary mixture is always based on isotope effects, i.e., on different properties of isotopic forms of a same molecular species. A single element where an elementary separating process, such as electrolysis, distillation, chemical exchange, or catalytic evolution and fuel cell oxidation (as in this work) is effected, is called a *separating unit*. It is schematically presented in Figure 1.

The separating unit, due to the separating agent, divides one feed stream into two outgoing streams (phases). It is a convention that the *heads stream* is partially enriched in the desired isotope (the product stream), while the *tails stream* is partially depleted (waste), although it depends on the aim. In the case a) these phases are: the water solution remaining in the reactor and the generated hydrogen leaving the unit, respectively. Analogously, in the case b) these phases are: water produced in the fuel cell and the incoming hydrogen at the cell, respectively.

A fundamental measure of the separation efficiency effected in a specified separating unit, the latter based on a selected process, is the *separation factor*  $\alpha$ . In cases of the separating processes exploited here, we defined  $\alpha$  as the ratio of isotope concentrations in the liquid phase – supposed to be enriched, and the hydrogen-gas phase – supposed to be depleted in deuterium, at the unit

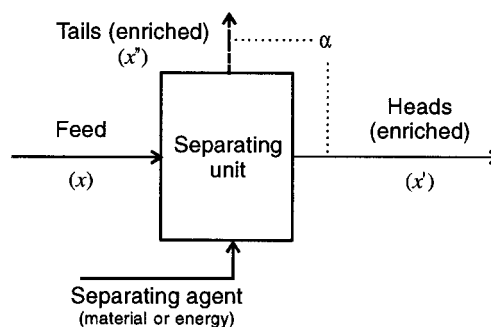


Figure 1. Schematic representation of a separating unit.  $x$ ,  $x'$ ,  $x''$  – the atom fraction of the desired isotope (D) in the specified stream (phase).

$$\alpha = \frac{x'}{1-x'} : \frac{x''}{1-x''} = \left( \frac{[D]}{[H]} \right)_{liq} : \left( \frac{[D]}{[H]} \right)_{gas} \quad (2)$$

where  $x'$  and  $x''$  are atom fractions of D in the liquid and hydrogen-gas phase,  $(1-x')$  and  $(1-x'')$  are corresponding fractions of H, respectively.  $[D]$  and  $[H]$  represent quantities of the isotopes expressed as concentrations.

a) We used the sodium tetrahydridoborate (borohydrate) fueled hydrogen generator HGen-E, Fractal Carbon, with the carbon monolith supported platinum reactor. The carbon monolith was in form of a disk 17 mm in diameter, 2 mm thick, with 8400 channels. Each channel (diameter of 80  $\mu$ m) has been coated with Pt-catalyst. Hydrogen produced in this way was passed over a silica-gel dryer to remove water vapor, and introduced into a sample cell for mass-spectrometric isotope analyses. The experimental setup used for this purpose is shown in Figure 2.

The Riedel de Haen sodium tetrahydridoborate of technical purity was used in all measurements. Commercial (Messer Griesheim), bottled gases

employed for FC were also of technical purity: hydrogen 99.9%, oxygen 99.7%.

b) For the experiments of hydrogen oxidation in FC we used membrane electrode assemblies (MEA) with an active area of 2 cm x 2 cm, produced by E-TEK, assembled in a two fuel cell stack. Membrane electrode assembly has a Pt loading of about 0.5 mg/cm<sup>2</sup>, using 20% Pt on carbon black (Vulcan XC-72) for anode and cathode. As membrane Nafion 115 was used. The experimental setup is shown in Figure 3.

Water produced on the cell is brought out with the excess oxygen and collected in the sample vessel for isotope analysis. Hydrogen was sampled at its exhaust on the other side of the cell.

An improved version of the VG Isogas (Model SIRA-12) mass spectrometer was used for isotope analysis of both, the liquid phase and the hydrogen gas evolved, in both types of experiments. The hydrogen gas samples were introduced directly into the spectrometer, while the water ones were previously transferred to hydrogen via reduction on the zinc catalyst

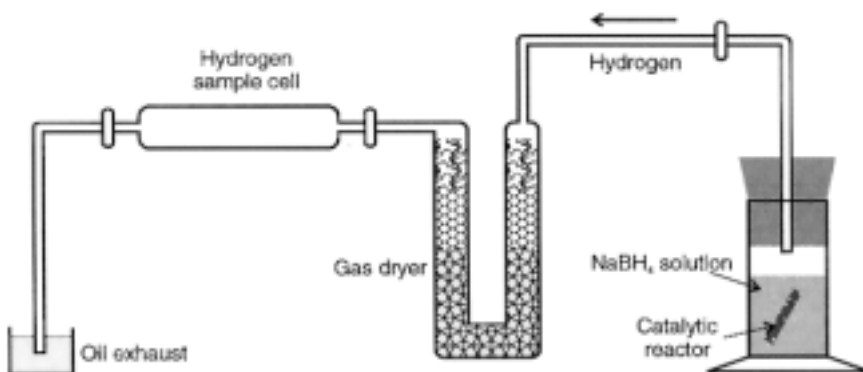


Figure 2. Schematic representation of the experimental apparatus used for generating and sampling hydrogen from the sodium tetrahydridoborate solution.

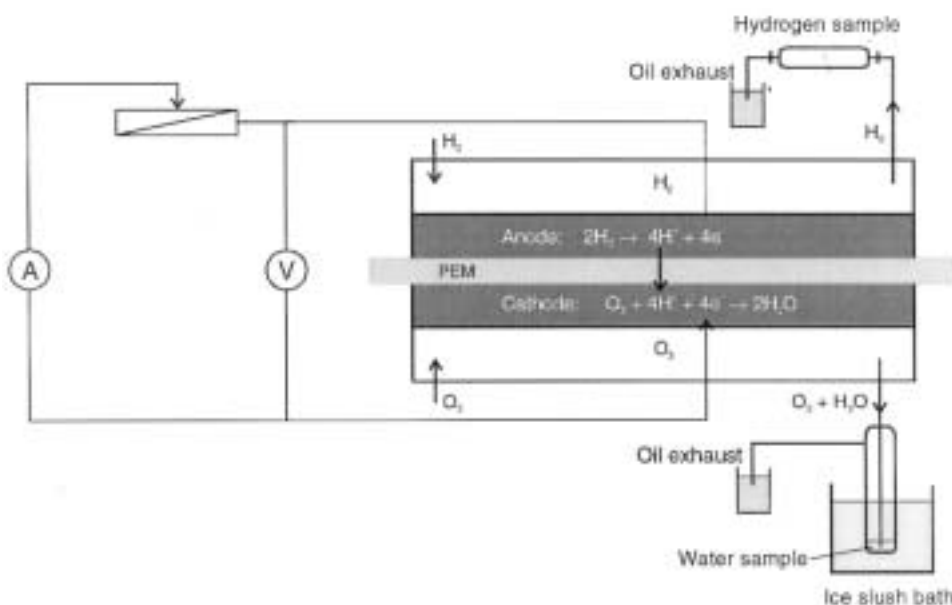


Figure 3. Schematic representation of a single PEM fuel cell experimental setup for measuring isotope separation factors.

at about 500°C, prior to introduction to the instrument. Same procedure was applied for the water solution of sodium tetrahydridoborate samples.

## RESULTS AND DISCUSSION

a) All experiments were carried out at room temperature (21–22°C). There were three runs with NaBH<sub>4</sub> concentrations of 5.30, 6.40 and 5.66 mass%, respectively. Rates of hydrogen evolution, which depends not only on the concentration of the solution but also on the quantity of the catalyst, were between 30 cm<sup>3</sup>min<sup>-1</sup> and 40 cm<sup>3</sup>min<sup>-1</sup>. Deuterium contents in the streams and corresponding isotope separation factors are shown in Table 1.

Table 1. D/H isotope separation factors obtained with the Pt-catalyst based water–NaBH<sub>4</sub> hydrogen generator at room temperature

Run number	Run duration (min)	Rate of hydrogen evolution (cm <sup>3</sup> min <sup>-1</sup> )	D-content		α
			10 <sup>6</sup> · x' (liquid)	10 <sup>6</sup> · x'' (hydrogen)	
1	120	30–40	155	34	4.6
2	240			34	4.6
3	200			22	7.0
Average:					5.4

Deuterium content in the remaining solution was found to be 0.000155 (155 ppm). Prior to the isotope analysis the solution had to be quantitatively distilled in vacuum, to extract pure water from it to be subjected to further processing. As expected, D-content was not changed too much relative to the natural level during runs (146.2 ppm), as the quantity of the solution was much bigger than the quantity of the evolved hydrogen.

b) The experiments were carried out at room temperature (21–22°C). We performed three relatively long runs, in which up to 2 g of water were collected for isotope analysis. Rates of hydrogen and oxygen flows were about 50 cm<sup>3</sup>min<sup>-1</sup> and 21 cm<sup>3</sup>min<sup>-1</sup>, respectively, in both runs. These rates were kept constant once the highest values of the electrical parameters of the cell were achieved. After that, except in the first run, these parameters changed continuously toward higher powers released. That is probably a matter of getting at a stationary state. We displayed here only the start and end values. The results are shown in Table 2.

It is quite interesting that we obtained very low D-concentration in the hydrogen leaving the fuel cell for all runs. Actually, it was too low to be measured precisely with the input hydrogen used. In some measurements we obtained D-content as low as 5 ppm. However, our estimation was that the error at this level could be several times the value displayed. Anyhow, the estimated isotope separation factor was at least 12, which is a surprisingly high value. It gave us a strong evidence of the isotope effect. The proper way to resolve the doubt would be in using the input gas more

Table 2. D/H isotope separation factors obtained using the E-TEK two fuel cell stack with Pt-catalyst and Nafion 15 membrane at room temperature. D-content in the input hydrogen = 74 ppm.

Run time (h)	U (V)	I (mA)	D-content		α	
			10 <sup>6</sup> · x' (liquid)	10 <sup>6</sup> · x'' (hydrogen)		
I	9.2	0.1	100–120	180	5–15	>12
II	16.8	Start	0.472	101	275	/
		End	0.641	137		
III	27.8	Start	0.52	128	225	/
		End	0.52	115		

concentrated in D, which would rise the D-contents of both output streams to easily measurable levels.

The results displayed in tables 1 and 2 clearly show that there are isotope effects in both investigated processes. As expected, deuterium always migrated to the dense (liquid) phase. The average value of the obtained separation factor for evolution of hydrogen in the water–NaBH<sub>4</sub> hydrogen generator, α = 5.4, can be considered as reasonable. They are typical for the Pt-catalyst, which is in this case not only the catalyst for the hydrogen evolution (a) or hydrogen oxidation reaction (b), but also for the isotope exchange reaction between water and hydrogen (H<sub>2</sub> + HDO → HD + H<sub>2</sub>O), taking place consequently. The room temperature value for the latter is α<sub>298K</sub> = 3.81 [5]. Thus, any primarily achieved separation efficiency will be conclusively settled to the value characteristic for the exchange reaction.

For comparison, the separation factors for most electrocatalytic methods of hydrogen evolution from alkaline electrolytes are much above the α-value for the exchange reaction [6]. Because of that the catalyst suitable for isotope enrichment in evolution processes should be made from a material indifferent to the isotope exchange, to retain the primary isotope ratio.

This work was an attempt to expose this important aspect of hydrogen energy in a fundamental manner, rather than to optimize the system. In that sense the Pt-catalyst was chosen as a typical, reference and very well investigated one, to show the effect. True optimization would primarily mean playing with different catalysts, along with adjusting the overall process conditions to obtain the best result. One possible direction could be investigation of catalysts that have already shown promising potential in water electrolysis from alkaline solutions [7]. Among them, special attention could be paid to those made as specific inter-metallic combinations of transition metals [8].

## CONCLUSION

This work was an attempt to expose hydrogen isotope effects to investigation in two specific *hydrogen-energy* transfers, not seriously taken into account up to now, and to develop approaches to their measurements.

We proved experimentally those effects, expressed through the isotope separation factors, and indicated their values at room temperature.

Obtained results are in accordance with expectations based on the nature of the processes and certain knowledge on some analogous systems.

#### ACKNOWLEDGMENTS

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Scepán S. Miljanić is a professor at the Faculty of Physical Chemistry of the University of Belgrade. He teaches Radiochemistry and nuclear chemistry.

He graduated from the Faculty of Sciences (Department of Physical Chemistry), University of Belgrade, in 1972. He received the M.Sc. degree in 1975 and Ph.D. degree in 1981, both in physical chemistry at the same university. He has spent twenty years doing research in the Vinca Institute of Nuclear Sciences, where he used to be the director of the Department of Physical Chemistry (1993-95). He worked at the University of California at Berkeley (1979-80) in the field of molecular relaxation, and MGU Moscow - 1986, and also had an official cooperation under the EU with the University of Strathclyde (Glasgow) and the Heriot Watt University (Edinburgh) onto a new concept of gas lasers.

His main research interest is in the chemistry of isotopes, primarily isotope effects, molecular relaxation in collisions and laser spectroscopy of isotopic species, along with the conventional methods of isotope separation (catalytic chemical exchange and electrolysis). He wrote the book titled *Hydrogen Isotope Effects - Heavy Water* (in Serbian), published in 1996.

He has been interested very much in the hydrogen energy concept, especially regarding the isotope effects, isotope separation and deuterium enrichment by electrolysis of water. Recently, he started working on those effects in other hydrogen transferring devices, like catalytic hydrogen generators and fuel cells.

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Born in Belgrade, Serbia & Montenegro. He graduated from the University of Belgrade, Faculty of Physical Chemistry in 2003. Since that time he has been employed as a research trainee at the Laboratory of Physical Chemistry of the Vinca Institute of Nuclear Sciences, Belgrade. His research activities have been focused on separation of the hydrogen isotopes and mass spectrometric analysis. He is now a postgraduate student of the Department of Physical Chemistry, University of Belgrade.

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##### Research interest

He is now the employ of the Vinca Institute of Nuclear Sciences - Laboratory of Physics, Belgrade, where he works on the application of carbon materials in fuel cell technology and modification of glassy carbon surface properties by high energy ion implantation.

In the past he worked about eighteen years for the Laboratory of Material Science of the same institute, where he was the Head of Carbon Research. His activities there covered the following fields: Modification of the surfaces of carbon materials in order to improve compatibility with living tissues and produce cheaper and stronger carbon-carbon composites; Investigation of the effect of hetero-atoms (Si, B, P, Ag) incorporated into the carbon and graphite materials, on structural and surface properties; Analysis of processes significant for production of carbon and graphite materials.

He also worked as the research assistant (1994-1997) for the Trent University, Department of Chemistry, Peterborough, Ontario (Canada), on computer simulation of ion trajectory in the quadrupole ion trap mass spectrometer.

As the visiting scientist he spent three years (1980-1983) at the Department of Metallurgy and Materials Technology, University College of Swansea, Swansea (Great Britain), examining physical and chemical processes involved in the pyrolytic carbon, glassy carbon and carbon-carbon composite formation, as well as on the biomedical application of carbon materials.

He patented silicon-carbide preparing procedure after observing silicon and carbon interaction.

