ISOTOPE EFFECTS IN:

a) CATALYTIC GENERATION OF HYDROGEN FROM SODIUM TETRAHYDRIDOBORATE
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 (NaBH₄), the sodium borohydride fueled hydrogen generator H₂gen-E, Fluidal 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 cm², 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 (α) 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: α(#H) = 5.4, α(4H)>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-known 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) – ¹H with an abundance of 99.985%, which is predominant and most common one; (ii) Deuterium – ²H (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 PWR type (in the form of heavy water), and possibly as a fuel component in fusion thermonuclear reactors of the future; (iii) Tritium – ³H (T) is a radioactive hydrogen isotope with an abundance of T/H = 1:10⁻¹⁶, (one T atom per 1 cm³ 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 tons 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 (NaBH₄) using a special catalyst. This process is commonly characterized by the rate of hydrogen evolution for the given catalytic reactor and the NaBH₄ 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
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. Anyway, 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 tetrachloridoborate (NaBH₄) 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 tetrachloridoborate (NaBH₄) reacts with water to form hydrogen and sodium metaborate (NaBO₂) according to the following mechanism:

\[
\text{NaBH}_4 + \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + \text{H}_2
\]

\[
\text{NaBO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaBH}_4 + 2\text{H}_2 \quad \Delta H = -217 \text{ kJ/mol}
\]

This reaction does not normally proceed spontaneously, and solution of NaBH₄ 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 hydroge ions, realising electrons and creating proton (H⁺):  

\[
2\text{H}_2 \rightarrow 4\text{H}^+ + 4e^-
\]

At the cathode, oxygen reacts with electrons taken from the electrode, and H⁺ ions from the electrolyte, to form water.

\[
\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}
\]

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:

\[
\text{The rate of water production} = \frac{9.38 \times 10^{-5} \cdot P_e}{V_c} \text{ kg s}^{-1}
\]

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 \( \rightarrow \) x' the atom fraction of the desired isotope (D) in the specified stream (phase).](image-url)
\[
\alpha = \frac{x'}{1-x'} : \frac{x''}{1-x''} = \left( \begin{array}{c} [D] \\ [H] \end{array} \right)_{\text{in}} : \left( \begin{array}{c} [D] \\ [H] \end{array} \right)_{\text{gas}}
\]

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 (borohydride) fueled hydrogen generator HGen-E, Frelad 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 µm) 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 analysis. 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 assemblies has a Pt loading of about 0.5 mg/cm², using 20% Pt on carbon black (Vulcan XC-72) for anode and cathode. As membrane Nation 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.](image)

![Figure 3. Schematic representation of a single PEM fuel cell experimental setup for measuring isotope separation factors.](image)
at about 500°C, prior to introduction to the instrument. Same procedure was applied for the water solution of sodium tetrahydropicotate samples.

RESULTS AND DISCUSSION

a) All experiments were carried out at room temperature (21–22°C). There were three runs with NaBH₄ 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 cm³/min⁻¹ and 40 cm³/min⁻¹. Deuterium content 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-NaBH₄ hydrogen generator at room temperature.

<table>
<thead>
<tr>
<th>Run number</th>
<th>Run duration (min)</th>
<th>Rate of hydrogen evolution (cm³/min⁻¹)</th>
<th>D-content</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>30–40</td>
<td>155</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
<td></td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td></td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>54</td>
</tr>
</tbody>
</table>

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 cm³/min⁻¹ and 21 cm³/min⁻¹, 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.

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.

<table>
<thead>
<tr>
<th>Run time (h)</th>
<th>U (V)</th>
<th>I (mA)</th>
<th>D-content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10⁻⁶ - x⁻¹</td>
</tr>
<tr>
<td>I</td>
<td>9.2</td>
<td>0.1</td>
<td>100–120</td>
</tr>
<tr>
<td>II</td>
<td>16.8</td>
<td>Start</td>
<td>0.472</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End</td>
<td>0.641</td>
</tr>
<tr>
<td>III</td>
<td>27.8</td>
<td>Start</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End</td>
<td>0.52</td>
</tr>
</tbody>
</table>

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-NaBH₄ 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 (H₂ + D₂O → H₂ + H₂O₂), taking place consequently. The room temperature value for the latter is α₁₀⁻₀ = 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 these 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.

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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.

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