

Test for additional heat evolution in electrolysis of heavy water with palladium cathode

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Calorimetric experiments, in which heavy water and ordinary water were subjected to electrolysis in a closed system with regeneration, have been carried out. No additional heat evolution was observed in the electrolysis of heavy water.

In late March and early April of this year, there were numerous reports of the observation of a low-temperature nuclear fusion in the electrolysis of heavy water with a palladium cathode. Some of these reports stated that there was a significant additional heat evolution (greater than the electrical energy expended) in the process.

In an effort to detect this heat evolution, we have carried out a calorimetric experiment on the electrolysis of heavy water in a closed system of constant composition (the gases which formed were returned to the original water through a catalytic reaction on a heated platinum wire). Under these conditions, no energy was stored in the products of the electrolysis, and the electrical energy which was supplied was converted completely into heat. If there was an additional heat evolution, the thermal power which was evolved should have exceeded the electrical power supplied. In order to eliminate sources of errors associated with differences in the measurement conditions, we determined the thermal equivalent of the electrical power supplied in an experiment which was completely identical except that we used ordinary water, in which by assumption there would be no additional heat evolution.

By virtue of the design of the experiments, the occurrence of an additional heat evolution exceeding the experimental error should have been manifested as a significant difference between the results obtained with heavy water and ordinary water.

In the experiments we used heavy water with a 98% deuterium concentration and doubly distilled ordinary water, to which we added respectively deuterated and ordinary lithium hydroxide, which was not subject to changes during the electrolysis. This additive was used to increase the electrical conductivity. The cathode was a thin-walled palladium tube in a vertical orientation ($D \approx 6$, $h \approx 8$, $d \approx 0.1$ mm). The anode, an unclosed cylinder of platinum foil, enclosed the cathode; the distance between electrodes was 3–4 mm. The platinum wire used for the regeneration of the water ($D = 0.05$, $l = 60$ mm) was wound into a spiral and positioned 15–20 mm above the surface of the solution. The solution covered the electrodes completely.

As the reaction vessel we used a glass cup hermetically sealed with a rubber cap, to which the electrodes and the spiral were attached. A thin-walled stainless-steel tube, which passed through this gap, was used to mount the reaction vessel and to monitor the pressure in it. The reaction vessel contained 18 ± 0.2 cm³ of water with the lithium hydroxide additive (0.8 mole/dm³).

As a quasiadiabatic calorimeter we used a silver-plated glass Dewar with a volume of about 2 dm³, equipped with a semihermetically sealed, heat-insulating cover of polystyrene foam. The calorimeter was partially filled with water; the reaction vessel, a thermometer, and a vaned stirrer ($D = 25$ mm) were immersed in the water. The stirrer was rotated by a stepping motor at a constant (within $\pm 1\%$) velocity of about 500 rpm. The heat evolution of this stirrer did not exceed 200 mW. The tube extending out of the reaction vessel passed through the cap of the calorimeter; its end was covered by a rubber elastic balloon, which demonstrated the pressure changes in the reaction vessel. Wadding was stuffed in the tube to oppose convection.

As the thermometer we used a silicon diode in a thin-walled nickel tube filled with toluene. A current of 1 mA was passed through the diode; the voltage drop across it was converted by a special circuit into a 50-mV/K analog signal. This signal was used, along with two comparators, to control a flip-flop circuit, which started and stopped an electronic timer with a precision of ± 1 s. The reference levels for the comparators were chosen in such a way that a comparator was triggered if the temperature in the calorimeter reached 293.2 K, while stopping occurred at 303.2 K (the reproducibility of the temperature interval $\Delta T = 10$ K was better than 0.1%).

The electrolyzer was supplied power from a special dc power supply which maintained a constant output power in the face of changes in the load current. This power supply was connected to the calorimeter in a four-conductor arrangement in order to eliminate the power which was evolved in the leads, and which depended on the load current. This power supply was constructed on the basis of a proportional-plus-integral controller. A signal proportional to the power was generated from the voltage and current signals by means of an analog multiplier. According to tests with dummy loads, the output power (10 W) was stabilized within 0.02% over the working current range of 1.5–2.0 A.

Experiments were carried out on this apparatus for 10 days in series of two to five, without a change of the solution in the reaction vessel. Experiments with heavy and ordinary water were alternated in a random pattern. In the course of the experiments, the ambient temperature was in the interval 293.7–295.7 K (an experimental estimate of the extent to which the calorimeter was not perfectly adiabatic revealed that a 1-K change in the ambient temperature introduced an error of 0.2% in the result of an experiment). Before the measurements, 1000 cm³ of water at a temperature of 290–292 K was poured into the calorimeter (the amount of water was reproducible within 0.05%). The stirrer was then turned on, and a current was passed through the electrodes. The platinum spiral was initially connected in parallel with the electrodes; after 2–3 min it was disconnected. It remained in a heated state (at about 1000 K) by virtue of the heat of the catalytic reaction. A quasisteady regime was established in the calorimeter in 3–5 min. The timer was then started and stopped automatically when the control temperatures were reached. The result of an experiment was the timer reading Δt , which served as a measure of the thermal power that was evolved in the calorimeter: $\Delta t = c\Delta T/P$, where c is the heat capacity of the calorimeter. The pressure in the reaction vessel did not increase noticeably in the course of an experiment; i.e., electrolysis products did not accumulate.

We carried out seven measurements with heavy water and ten with ordinary

water. The relative mean square error of an individual measurement was less than 0.2%. Since the heat capacities of the calorimeter with the samples of heavy and ordinary water differ slightly because of the difference in the heat capacities of the samples themselves, we calculated the corresponding correction: $\Delta\Delta t \approx 9$ s (in this calculation we used tabulated values of the heat capacities¹ and densities² of heavy and ordinary water). After this correction was made, the average values for the ordinary water and the heavy water turned out to be $\overline{\Delta t}_o = 4528$ s and $\overline{\Delta t}_h = 4530$ s. Unaveraged data were used to test the hypothesis that there was no additional heat evolution during the electrolysis of the heavy water. In view of the experimental design, this hypothesis is equivalent to the hypothesis that the samples $\Delta t_{o,1} \cdots \Delta t_{o,10}$ and $\Delta t_{h,1} \cdots \Delta t_{h,7}$ belong to a common general set. The latter hypothesis was tested on the basis of the Wilcoxon test,³ which does not require the use of any assumption regarding the nature of the distribution function. This test showed that the hypothesis does not contradict the experimental data.

In summary, under the conditions of these experiments, and with allowance for the accuracy achieved, we did not observe additional heat evolution during electrolysis of heavy water with a palladium cathode.

¹I. K. Kikoin (editor), *Handbook of Tables of Physical Quantities*, Atomizdat, Moscow, 1976.

²A. I. Efimov *et al.*, *Handbook on Properties of Inorganic Compounds*, Khimiya, Leningrad, 1983.

³I. N. Bronshtein and K. A. Semendyaev, *Mathematics Handbook for Engineers and Engineering Students*, Nauka, Moscow, 1981.