

DETERMINATION OF THE EXCESS ENERGY OBTAINED DURING THE ELECTROLYSIS OF HEAVY WATER

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COLD FUSION

TECHNICAL NOTE

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The total heat balance during the electrolysis of D₂O with a palladium cathode is determined by placing the entire hermetically sealed electrolysis system (the electrochemical cell connected with a vessel of varying volume) in an isoperibolic calorimeter. Significant excess power density (excess specific rate of heating) is obtained even though a palladium cathode of thin wire (0.05-cm diam) is used, in which case a relatively low value of excess energy is expected. The method and arrangement applied remove the main causes of inaccuracies in determining the excess energy. Thus, the possibilities of using this energy seem to be greater than some researchers are inclined to consider.

INTRODUCTION

Some successful measurements of the excess energy obtained during the electrolysis of heavy water, claimed by Fleischmann and Pons,¹ are reported.

The exact determination of the quantity of heat released during the electrolysis of heavy water requires consideration of various possible causes of incorrect results, including the following:

1. Gases leaving the electrolytic cell or blown through it during electrolysis usually remove some heat through temperature increase and water evaporation. This heat may be comparable to or even greater than the excess energy, especially if the possibility of superheated gases and supersaturated D₂O vapors is considered.

2. Uncontrolled absorption and desorption of D₂ may occur.

3. Uncontrolled interaction between D₂ and O₂ may take place.

4. There may be direct heat transfer between the electrolytic cell, which is heated during the electrolysis, and the medium surrounding the calorimeter.

5. The calorimetric liquid may be improperly stirred, which enables heat to be removed from the calorimeter.

6. Inefficient stirring can cause unequal temperatures in the different regions of the calorimetric liquid.

7. A decrease or increase in the quantities of gases dissolved in the calorimetric liquid may have a measurable effect.

8. A change in the gas-phase pressure in the calorimeter may have a measurable influence on the result.

9. Processes other than those already mentioned may take place in the calorimeter, inside the electrolytic cell, or outside, together with the electrolysis of D₂O.

10. Energy expenditure or gain may be connected with changes in the palladium cathode (volume, cracking, oxidation, etc.).

Most of these possible causes of errors in the excess heat measurement seem to exist to a certain extent in the studies carried out so far. This paper presents a method to more accurately determine the excess energy and if possible to eliminate some of the possible explanations for the excess energy.

EXPERIMENTAL

In our study of the excess energy generated during electrolysis of heavy water, we used the calorimeter shown schematically in Fig. 1. It consists of an opaque dewar vessel (1) hermetically sealed with a stopper (2), in which a quantity of double-distilled water (3) is contained. The electrolytic cell (4) is entirely submerged in the distilled water. It consists of a test tube (5) hermetically sealed with a stopper (6) containing metal parts (7). The electrolytic cell is connected with a vessel (8) of a varying volume (a plastic bubble) through a spiral metal tube (9). Above and under the electrolytic cell, two copper-constantan thermocouples (10 and 11) are welded (the upper weld is used only for control). A magnetic stirrer (12) is located on the bottom of the dewar vessel. The leads (13 through 19) of the electrolytic cell, thermocouples, and the resistor (20) (for determination of heat capacity) pass through the stopper of the dewar vessel. All the wires (thermocouples, electrode, and resistor leads) situated in the dewar vessel are insulated.

The cathode is made of 0.05-cm-diam × 32-cm-long palladium wire (Koch-Light Laboratories, 99.99% pure) weighing 0.76 g, which is wrapped in a zigzag manner into an

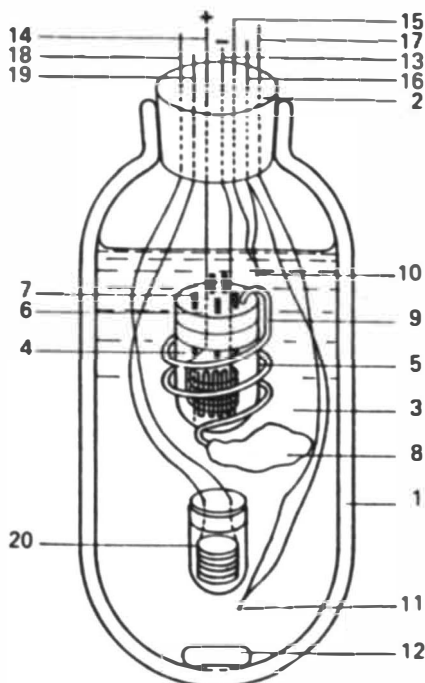


Fig. 1. Schematic of the calorimeter. See text for details.

–1.5-cm-long bundle of 21 wires. The anode is a platinum wire spirally wound around the cathode. The anode and the cathode are separated by a perforated Teflon tube.

The cathode is saturated with deuterium by a lengthy pre-electrolysis. During this time, the open cell is placed in a constant-temperature bath. The electrolytic cell contains 3 ml D₂O (Merck, 99.7% pure) plus ~0.01 M K₂SO₄. The D₂O is replenished regularly during the pre-electrolysis. The cell temperature is not measured during this time.

To begin the experiment, the pre-electrolysis current is stopped, the cell is removed from the constant-temperature bath, and it is assembled in the configuration shown in Fig. 1. The initial volume of the plastic bubble is measured in order to determine when the palladium cathode is saturated with deuterium. The cathode is ready (in the absence of electrolysis) for the experiment when the volume of D₂ + O₂ gas in the cell is constant with time: The deuterium is no longer being adsorbed nor desorbed by the cathode. The measurements begin when the temperatures of the cell and the calorimetric liquid are equal. Thus, we wait for >10 min after assembly of the apparatus.

We obtained the volume of the gases produced during the electrolysis by measuring the weight (volume) of water removed by the plastic bubble before and after the electrolysis. From this, we determined the character of the electrochemical reaction: possible absorption or desorption of D₂ by the palladium cathode, an interaction between D₂ and O₂, or other factors. (When the volume of the D₂ + O₂ did not correspond to the reaction of D₂O decomposition, the excess heat measurement was considered unsuccessful.)

A constant current *I* for the electrolysis of D₂O was ensured by a potentiostat-galvanostat PAR 273 serving as a galvanostat. The current was also controlled by a Hewlett-Packard 3465 B digital multimeter of ±1 × 10⁻⁴ A accuracy. The voltage was registered continuously by a Sony-Tektronix 336 digital storage oscilloscope; the accuracy of the voltage

measurements below 10 V was ±0.08 V, while for measurements in tens of volts the accuracy is ±0.8 V. The time Δτ = τ₂ – τ₁ of electrolysis measured by the oscilloscope was simultaneously measured by a Casio fx-7100 scientific calculator of ±0.01-s accuracy. After the completion of each experiment, the data from the oscilloscope's memory were dumped through a GPIB (IEEE 488) interface bus into the memory of an Apple IIe microcomputer, and the mean value \bar{E} of the applied voltage *E* during the experiment was determined through numerical integration of the multiple voltage values acquired during the continuous monitoring of the voltage throughout the whole process.

The temperature of the calorimeter (thermoemf of the thermocouples) during the experiments was read at 30-s intervals using a Hewlett-Packard 3465 B digital multimeter of 1 × 10⁻⁶ V accuracy. The thermocouples were calibrated using a thermostat. It was determined that 39-μV thermoemf corresponds to 1°C.

RESULTS AND DISCUSSION

Results from the experiments are presented in Figs. 2, 3, and 4.

In Fig. 2, the temperature (thermoemf) as a function of time is shown before, during, and after passage of a 0.5990-A current through the resistor for 181.25 s at 9.76 V. From these data, the heat capacity of the calorimeter is determined to be *K* = 841 J · grad⁻¹.

In Fig. 3, the voltage-time curve [*E* = *E*(τ)] is taken before, during, and after passage of a 0.1280-A current through the electrolytic cell for an interval Δτ = τ₂ – τ₁ = 181.32 s. The mean voltage obtained from Fig. 3 is \bar{E} = 44.0 V.

When using these data for *I*, *E* = *E*(τ), and Δτ = τ₂ – τ₁, the energy spent for the electrolysis of D₂O is obtained from the Joule's law:

$$W = I \int_{\tau_1}^{\tau_2} E(\tau) d\tau = I\bar{E}\Delta\tau = 1020 \text{ J .}$$

In Fig. 4, the temperature as a function of time taken before, during, and after the electrolytic process is shown. The increase in the calorimeter temperature due to electrolysis is

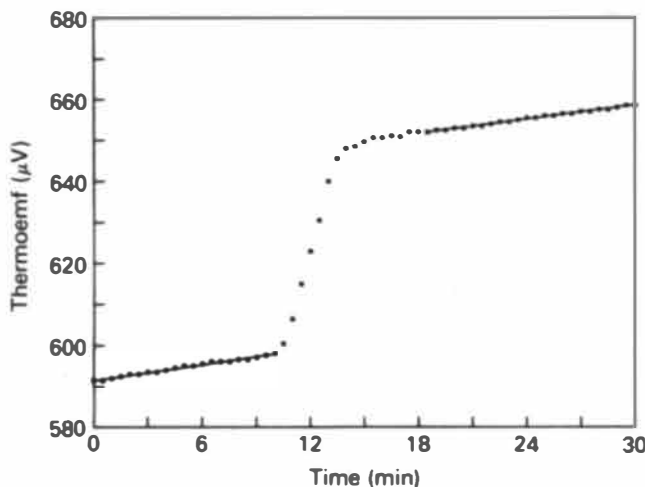


Fig. 2. Temperature (thermoemf) as a function of time for determination of heat capacity of the calorimeter.

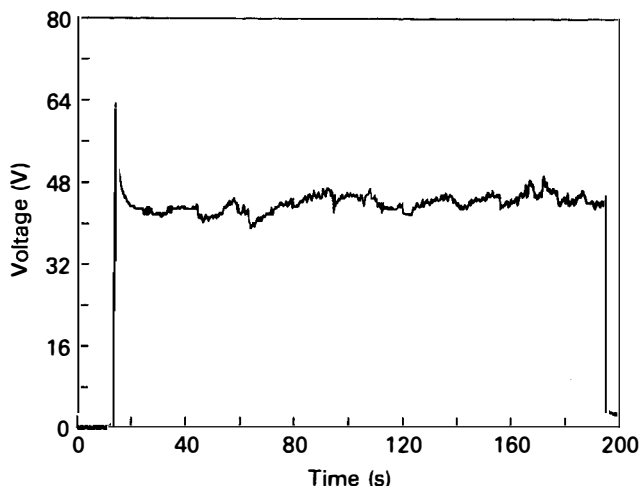


Fig. 3. Cell voltage as a function of time during electrolysis.

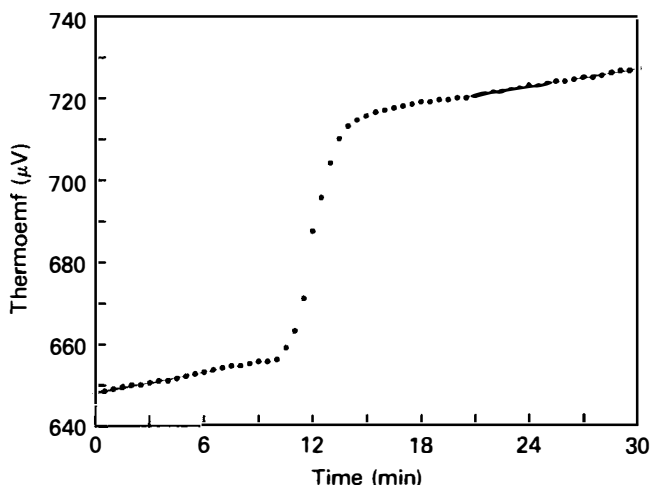


Fig. 4. Temperature (thermoemf) as a function of time during the experiment.

found to be $\Delta t = 1.44^\circ\text{C}$. The temperature time dependence before and after electrolysis should coincide with the dependence taken when no current is passing through the system. This is the characteristic time dependence of the rate of heat dissipation from the given system toward the ambient under the given conditions. The quantity of heat Q obtained during electrolysis is

$$Q = K\Delta t = 1210 \text{ J} .$$

To compare the energy obtained with the energy spent, it is necessary to remember that the energy we obtain consists not only of the experimentally measured heat (1210 J) but also of the chemical energy that can be released if the D_2 and O_2 gases produced during the electrolysis of D_2O inversely interact (recombine) to form D_2O again. It can even be stated that this chemical energy is usually the only useful energy that results from the electrolysis of heavy water. The available data from the handbooks are generally used: This energy has been established² as $\Delta H = -70.4133 \text{ Kcal/mol} =$

-294.6 KJ/mol at 25°C . Nevertheless, this quantity should be measured directly.

The use of an internal recombiner, however, is not the most suitable for proving the existence of excess heat. An active recombiner shifts the stationary state at which the palladium cathode is saturated (possibly supersaturated) with deuterium toward another stationary state at which the palladium cathode is undersaturated with deuterium. This occurs because the active recombiner recombines virtually the entire available quantity of oxygen and deuterium, both the quantity being evolved and the quantity existing in the liquid and the vapor phases. Underpressure (slight vacuum) in the system indicates this additional recombination. Thus, the diffusion of the D_2 toward the recombiner competes with its diffusion toward the bulk of the cathode and makes saturation impossible. As has been pointed by a number of authors,¹ saturation (even supersaturation) of the cathode with deuterium is a necessary condition for the observation of excess energy. Thus, it can be concluded that whenever excess power is observed in a cell with a recombiner the effect will be only conservative. Failure to observe excess energy in recombination cells, on the other hand, cannot be considered convincing proof of the impossibility of the system's producing excess energy. Further experiments are necessary to overcome this disadvantage of the recombiner.

On the basis of the mentioned current and time values, it is determined that during the electrolysis $1.2 \times 10^{-4} \text{ mol}$ D_2O is decomposed. The D_2 and O_2 gases thus obtained can interact inversely (recombine) to release energy of $1.2 \times 10^{-4} \times 294\,600 \approx 35 \text{ J}$. This energy should be added to the obtained heat. Note also that the quantity of gases measured using the vessel of varying volume (the plastic bubble) exactly corresponds to the expected volume calculated from Faraday's law. This observation invalidates the possible trivial explanation of the excess energy effect put forward in Refs. 3, 4, and 5. Thus, in our case the total energy obtained is $1210 + 35 = 1245 \text{ J}$, which exceeds by 225 J the amount of energy spent (1020 J).

When $\text{H}_2(\text{D}_2)$ is obtained electrochemically to be used as fuel, and when the question relates to the significance of hydrogen for energetics, only quantities such as the mentioned 35 J are taken into account. The energy losses due to overcoming the ohmic resistance of the solution, the leads, the electrodes, and the contacts are not considered because, in principle, these losses, which are significant in our case, are preventable to a great extent. The losses due to overcoming the D_2 and O_2 evolution overpotentials can also be disregarded because these overpotentials can be decreased,⁶⁻⁸ even eliminated, as in the case of Ref. 9. The only energy expenditure that is inevitable and cannot be decreased is the quantity necessary for the electrolytic process itself [decomposition of $\text{H}_2\text{O}(\text{D}_2\text{O})$]. In the ideal case, we reckon that the obtained chemical energy when using $\text{H}_2(\text{D}_2)$ as fuel is 100% versus the energy spent for the decomposition of $\text{H}_2\text{O}(\text{D}_2\text{O})$. In the present case, the amount of energy that can be used ($225 + 35 = 260 \text{ J}$) is more than seven times the usable energy expected from the electrolysis (35 J). This significant excess energy cannot be connected with the electrochemical process of decomposition of $\text{H}_2\text{O}(\text{D}_2\text{O})$ or with any other electrochemical or chemical process.¹

From the above data, it is seen that during the ~3-min electrolysis for the decomposition of $1.2 \times 10^{-4} \text{ mol}$ D_2O and for obtaining the respective quantities D_2 and O_2 , 35-J energy is spent while the total available energy (excess enthalpy + enthalpy of the obtained D_2 and O_2) is 260 J. That

TABLE I
Momentary Values of Excess Enthalpy Obtained During the Electrolysis of D₂O

Experiment	Electric Energy Spent for the Electrolysis (J)	Total Energy Obtained (Heat + Enthalpy of Obtained D ₂ and O ₂) (J)	Excess Rate of Heating (Excess Power) (W)	Excess Specific Rate of Heating (Excess Specific Power) (W/cm ³)
1	921	1130	1.15	18.3
2	830	910	0.431	6.85
3	1090	1210	0.662	10.5
4	856	910	0.298	4.73
5	835	885	0.276	4.37
6	1440	1560	2.61	41.4
7	777	869	0.508	8.06
8	1115	1134	0.104	1.66
9	937	961	0.132	2.10
10	873	961	0.481	7.64

is, for the 181.32-s electrolysis, a mean power of 0.2 or 3.2 W/cm³ Pd is spent for the decomposition of D₂O while the electrolytic cell has acted as an energy source (heat + chemical energy) of 1.43 W, which is 22.8 W/cm³ Pd. If only the excess energy (225 J) is considered, 1.24 or 19.7 W/cm³ excess power is available.

Table I presents data from some successful determinations of the excess heat obtained during the electrolysis of D₂O. Experiments 4, 5, and 6 were carried out on the same day at different times. The mean time interval between the experiments, except for experiments 4, 5, and 6 but including the intervals between them and the neighboring experiments, is ~110 h. The cathode current density for all the experiments except experiments 1 and 6 was 26 mA/cm². For experiment 1 the current density was 20 mA/cm², while for experiment 6, it was 80 mA/cm². In all cases except for experiment 6, the electrolysis lasted ~3 min; for experiment 6, it lasted 46.00 s.

Our method and experimental arrangement give a possibility of precise determinations of the excess heat obtained during the electrolysis of D₂O, thus ensuring a categorical answer to the important question of whether the Fleischmann and Pons effect¹ exists and, if it does exist, the exact value of the excess power during the electrolysis. However, it should be kept in mind that a comparatively short electrolysis process was carried out here after a continuous pre-electrolysis. Therefore, every excess enthalpy value obtained is valid only for a relatively short time interval—tens of seconds up to ~3 min, which we conditionally consider here as only a moment (a randomly chosen moment), compared to the tens and hundreds of hours duration of the other studies of the excess energy. As seen from Table I, the momentary values of the excess power and the excess power density (excess specific rate of heating¹) obtained at different moments differ significantly from each other. While the result from experiment 6 is 2.61 W and 41.4 W/cm³, experiment 8 gave values of 0.104 W and 1.66 W/cm³, respectively, i.e., ~25 times lower values. Indeed, in experiment 6 three times greater current density was applied compared to experiment 8. In experiment 1, the current density was lower than in experiment 8; nevertheless, the values obtained for the excess power and excess power density in experiment 1 was 11 times greater than in experiment 8.

The data shown in Table I indicate that the momentary value of the excess power and excess power density do not depend on the current density. As is seen in the table, excess power density values of 1.66, 10.5, and 18.3 W/cm³ are observed for the same current density value (26 mA/cm²). In this experiment, the excess power density value is 19.7 W/cm³. Evidently, the momentary values of the excess power and the excess power density are random. Therefore, one can conclude that the mean values of the excess power and the excess power density from all the experiments carried out at 26 mA/cm² are 0.459 W and 7.29 W/cm³.

Since the errors from the measurements are sufficiently low and there are no significant heat losses, it cannot be accepted that the observed variation in the excess power density values is due to errors in the measurement. Therefore, it is likely that the phenomenon is of a sporadic nature. From our results, it can be concluded that the excess power and the excess power density values obtained over many hours by other authors are in fact the mean values of these quantities, which are the result of numerous differences in momentary values. Note that the moments for obtaining these values are chosen randomly.

The mean value of the excess power density obtained by us with a 0.05-cm palladium wire electrode at a current density of 26 mA/cm² is seven times greater than that¹ obtained after many hours with an electrode with a greater diameter (0.1 cm) and at a higher current density (64 mA/cm²). The hermetical sealing of the calorimeter, the submersion of the entire electrolytic cell into the calorimetric liquid, keeping the obtained gases and vapors in a cell of varying volume, and the other measures taken by us seem to ensure much lower losses of the obtained excess enthalpy.

The results presented in this technical note indicate that the possibility of the practical use of the excess energy resulting during the electrolysis of D₂O are greater than is sometimes considered.

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