

PRECISION CALORIMETRIC STUDIES OF H₂O ELECTROLYSIS

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Abstract

Calorimetric studies were undertaken of the heat, observed during the electrolysis of H₂O in normal open and closed cell as well, employing palladium cathode. A difference in heat observed during the process between opened and closed system was found. Heat generated under different conditions was presented as a function of the working current density or voltage. Such results were briefly discussed according to general thermodynamics and electrochemistry.

Keywords: calorimetry, electrolysis, 'excess heat', general thermodynamics

Introduction

Recently, much research work on the calorimetric measurement of electrolysis process of water (or heavy water) were reported, because it was believed that the electrolysis could induce a nuclear fusion [1-6]. Therefore, if the controlled nuclear fusion could be realized at room temperature a powerful and clear energy source could be obtained easily. As we know well, the project was started from an announcement made by Fleishmann and Pons who found the 'excess heat' generated in the electrolysis of heavy water in 1989. Since then there are many scientists, in the world, who are still trying hard to materialize this aspiration.

Now, one hopes to have clear answers on the following problems:

- a.) Does the 'excess heat', or 'anomalous heat' generated during the electrolysis process really exist?
- b.) Were these heat phenomena fabricated by some persons?(!)

Up to now, many scientists working in many laboratories in countries, such as USA, Japan, Italy, Russia and China, have carried out thousands of experimental runs in this field, and obtained results which may give a clear answer: the 'excess heat' can be obtained in the electrolysis of heavy water (even light

the 'excess heat' can be obtained in the electrolysis of heavy water (even light water)! But nobody can definitely give an incontestable answer: the excess heat generated during electrolysis of heavy water must be accompanied by convincing nuclear fusion.

In this case, it is very important to understand the processes causing the 'excess heat', or 'anomalous heat' generated during electrolysis of heavy (or light) water and the factors, such as the electrolysis current, affect heats taking place.

Experimental

Calorimeter

A Calvet type of microcalorimeter was also used in this work. Figure 1 shows a schematic diagram of the electrolysis cell, and the experimental circuit in the open system. A microcomputer was used to acquire and digitize the experimental and the reference signals at millisecond intervals from the thermopile of the calorimeter. It was also used to register the electrolysis voltage and current at the same time intervals.

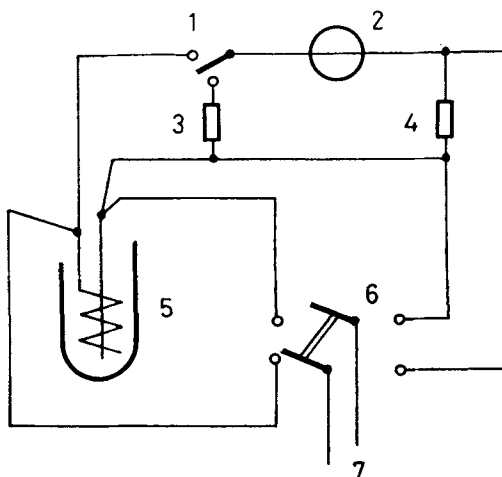


Fig. 1 Experiment circuit. 1-Kw2; 2-power supply; 3-simulated resistance; 4-standard resistance; 5-electrolysis cell; 6-Kw1; 7-to the recorder/computer

Electrolysis cell and calorimetric chamber

The closed system

Figure 2 shows the closed electrolysis cell. It was constructed of glass with an internal diameter of 1.4 cm and height of 7.2 cm. The cell contained 2.5 ml of 0.1 M NaOH solution. The palladium (>99.9%) rod was used for cathode and the platinum (>99.9%) wire for anode as before [5]. The cell was sealed

with a rubber stopper 1 cm thick which incorporated feedthroughs for the electrical connections to the anode and cathode, and a fine Teflon tube filled with sufficient water. The tube was used to close the cell system and to monitor the change of pressure in cell. Recombination of the evolved hydrogen and oxygen in this work was achieved using a ball of very fine Pt wire platinized. Before the calorimetric experiments of electrolysis running it should be sure that the recombiner works without pressure change in the electrolysis cell during the operation of it at high (at least higher than 40 mA) current over several weeks. Manganin wire was coiled on the cell to be a calibration heater. The cell with the heater coil was placed in a gilded copper cylindrical vessel filled with silicon oil.

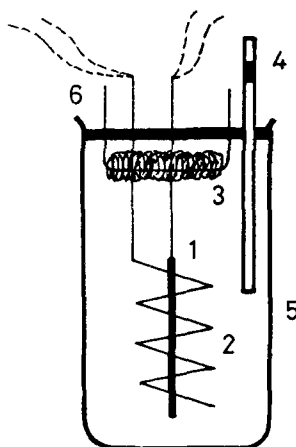


Fig. 2 Diagram of electrolysis cell. 1-Pd cathode; 2-Pt anode; 3-recombiner catalyst; 4-TTFE pipe; 5-glass tube; 6-rubber plug

The open electrolysis system

The construction of electrolysis cell used in the open system was totally the same as that in the closed system but without recombiner and with an empty outlet tube.

Procedure

Calibration of calorimeter

The microcalorimeter was calibrated by applying varying amounts of electrical power to the coil heater and measuring the resulting changes of thermoelectromotive force (T.E.F) from the calorimeter with microcomputer acquisition and digitalization system (D). The calibration constant E (D/mW) of the microcalorimeter was thus determined. It was found that the calibration curve of D vs. input power was linear over range 0.6–48 mW (Fig. 3).

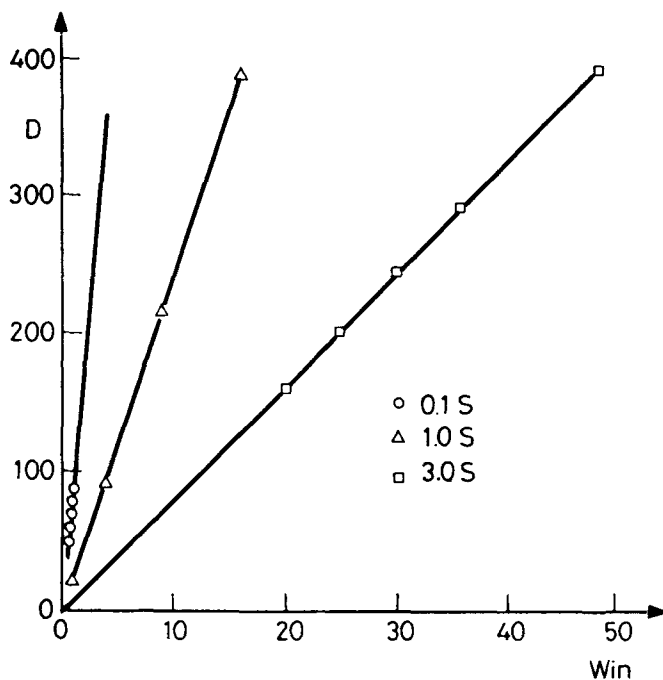


Fig. 3 Calibration of calorimeter

Electrolysis

An electric power pulse, with intervals wide enough to obtain experimental results, was produced in the electrolysis system. The electrolysis voltage applied on cell was in the range of 1.81 to 3.92 V, and electric current density was changed from 7.95 mA/cm² to 38.6 mA/cm², in the closed system. In the open system the cell voltage applied was varied from 1.81 to 2.83 V, and the current density was changed from 3.1 mA/cm² to 32.1 mA/cm². In the calorimetric measurements of electrolysis of heavy water, the cell voltage used was varied from (3.51±0.13) V to 5.98±0.48) V, and the current density was varied from 1.90 mA/cm² to 5.70 mA/cm².

Results and discussion

The closed system

The results of the heat measured by microcalorimeter during electrolysis in closed system and the electric work input into the electrolysis cell are presented in Table 1. Each of the ratio of heat measured to electric work input vs. the current density during the electrolysis is almost equal to 1.0. It is very clear that

there is no change in the ratio. Therefore, no excess heat was observed during the electrolysis of water in the closed system.

Table 1 Results of electrolysis of H₂O with Pt catalysts in closed system*

I_{in} / mA	$\sigma_{in} / \text{mA}\cdot\text{cm}^{-2}$	V_{ce} / V	$\Delta_{ce} / \mu\text{V}$	W_{in} / mW	W_{me} / mW	W_{me} / W_{in}
0.50	7.95	1.81	20.97	0.92	0.90	0.98
0.50	7.93	1.84	21.92	0.92	0.96	1.04
1.07	16.9	2.02	48.89	2.15	2.05	0.95
1.07	17.0	2.03	51.70	2.17	2.17	1.00
2.03	32.3	2.17	117.50	4.41	4.85	1.10
2.03	32.3	2.17	101.72	4.41	4.21	0.95
2.50	39.8	3.94	240.51	9.85	9.85	1.00
2.43	38.7	3.92	233.63	9.52	9.57	1.01

Ael. (shown the area of electrode used) is 0.0628 cm²

*After initial charging of Pd cathode over 500 h, these results were obtained without monitoring the H/Pd of the electrode.

The open system

In the electrolysis of H₂O

Table 2 shows that the same ratio, as mentioned above, of power measured (W_{me}) by calorimeter to electrical power (W_{in}) released into the electrolysis cell system as Joule heating in open system varies with the electrolysis current density.

The curves (— □ —, — Δ —, — × —) shown in Fig. 4 represent the results of the ratio.

The value of W_{in} was calculated using a common method [1] from the equation

$$W_{in} = I(E_{ce} - E_{th}) \quad (1)$$

where I is the cell current, E_{ce} is the potential difference across the cell and E_{th} in the thermoneutral potential for the electrolysis of water. The value of E_{th} for H₂O at 25°C is 1.48 V and 1.53 V for D₂O. It was found that there is a clear nonlinear relationship between the ratio and the electrolysis current density. By the usual calculation, the excess power (W_{ex}) should be given by

$$W_{ex} = W_{me} - W_{in} \quad (2)$$

The results of the excess power are shown in Table 3. It is clear, from Table 3, that the excess power generated during electrolysis of H₂O in the open system varies with the current density (or voltage).

In the electrolysis of D₂O

Table 4 shows the results obtained in the electrolysis of D₂O. The increase in the excess heat with current density is conspicuous.

Energy consumption in electrolysis of water

The cell voltage is a complex quantity made up of a number of terms [7], i.e.

$$E_{cc} = (E_c - E_a) + \eta_a + \eta_c + \eta_{mt} + IR_{cc} = E_{rev} + \eta_a + \eta_c + \eta_{mt} + IR_{cc} \quad (3)$$

Table 2a Results of electrolysis of H₂O in open system**

I_{in} / mA	$\sigma_{in} / \text{mA}\cdot\text{cm}^{-2}$	V_{cc} / V	$\Delta_{cc} / \mu\text{V}$	W_{in} / mW	W_{me} / mW	W_{me} / W_{in}
0.201	3.20	1.814	35.91	0.067	0.41	6.13
0.194	3.28	1.822	34.61	0.066	0.39	5.95
0.347	5.52	2.001	48.24	0.181	0.56	3.10
0.351	5.58	2.001	48.55	0.183	0.56	3.06
0.498	7.92	2.047	51.29	0.282	0.59	2.09
0.502	7.98	2.047	50.24	0.285	0.58	2.04
0.645	10.30	2.126	58.00	0.417	0.68	1.63
0.650	10.30	2.132	59.03	0.424	0.69	1.63

Ael. (shown the area of electrode used) is 0.0628 cm²

**After initial charging of Pd cathode over 500 h, these results were obtained without monitoring the H/Pd of the electrode.

Table 2b Results of electrolysis of H₂O in open system**

I_{in} / mA	$\sigma_{in} / \text{mA}\cdot\text{cm}^{-2}$	V_{cc} / V	$\Delta_{cc} / \mu\text{V}$	W_{in} / mW	W_{me} / mW	W_{me} / W_{in}
0.792	12.6	2.087	82.65	0.481	0.98	2.04
0.795	12.6	2.087	82.01	0.483	0.97	2.00
1.014	16.1	2.324	107.86	0.856	1.28	1.49
1.008	16.0	2.362	108.31	0.889	1.29	1.45
1.502	23.9	2.638	189.84	1.739	2.28	1.32
1.505	23.9	2.604	193.90	1.690	2.33	1.37
1.747	27.8	2.677	227.97	2.091	2.75	1.32
1.752	27.9	2.561	221.59	1.890	2.67	1.41
2.013	32.0	2.835	310.18	2.728	3.75	1.37
2.017	32.1	2.193	279.98	2.890	3.38	1.16

Ael. (shown the area of electrode used) is 0.0628 cm²

**After initial charging of Pd cathode over 500 h, these results were obtained without monitoring the H/Pd of the electrode.

Table 2c Results of electrolysis of H₂O in open system**

I_{in} / mA	$\sigma_{in} / \text{mA}\cdot\text{cm}^{-2}$	V_{ce} / V	$\Delta_{ce} / \mu\text{V}$	W_{in} / mW	W_{me} / mW	W_{me} / W_{in}
0.198	3.15	1.770	25.92	0.06	0.28	4.67
0.195	3.10	1.823	26.00	0.07	0.29	4.14
0.350	5.56	2.007	38.18	0.18	0.43	2.39
0.347	5.52	2.003	38.15	0.18	0.43	2.39
0.498	7.92	2.048	44.14	0.28	0.51	1.82
0.502	7.98	2.051	45.01	0.29	0.52	1.79
0.653	10.40	2.126	45.24	0.42	0.63	1.50
0.802	12.80	2.244	72.19	0.61	0.85	1.39
0.809	12.80	2.246	73.14	0.62	0.86	1.39
0.994	15.80	2.402	98.43	0.92	1.17	1.27
1.001	15.90	2.402	98.97	0.92	1.17	1.27
1.243	19.80	2.676	140.96	1.49	1.69	1.13
1.252	19.90	2.556	138.40	1.35	1.65	1.22
1.500	23.80	2.756	181.05	1.91	2.17	1.10
1.497	23.80	2.795	183.78	1.97	2.21	1.12

Ael. (shown the area of electrode used) is 0.0628 cm²

**After initial charging of Pd cathode over 500 h, these results were obtained without monitoring the H/Pd of the electrode.

where E_a and E_c are the equilibrium potentials for the anode and the cathode reactions respectively. The subscripts c , a and mt refer respectively to the activation overvoltages at the cathode and anode, and the polarization overvoltage due to mass transport of gaseous products away from the electrode surfaces. R_{ce} is the cell resistance. The total energy consumption is

$$W_{ce} = IE_{ce} \quad (4)$$

Table 3 Results of electrolysis of H₂O in open system

I_{in} / mA	$\sigma_{in} / \text{mA}\cdot\text{cm}^{-2}$	E_{cell} / V	W_{me} / mW	W_{in} / mW	W_{ex} / mW
0.201	3.20	1.814	0.41	0.07	0.34
0.502	7.98	2.047	0.58	0.29	0.29
0.792	12.6	2.087	0.98	0.48	0.50
1.014	16.1	2.324	1.28	0.86	0.42
2.013	32.0	2.835	3.75	2.73	1.02

W_{me} is a heat measured by calorimeter; $W_{in} = (E_{ce0} - E_{th}) \cdot I_{in}$; $W_{ex} = W_{in} - W_{me}$

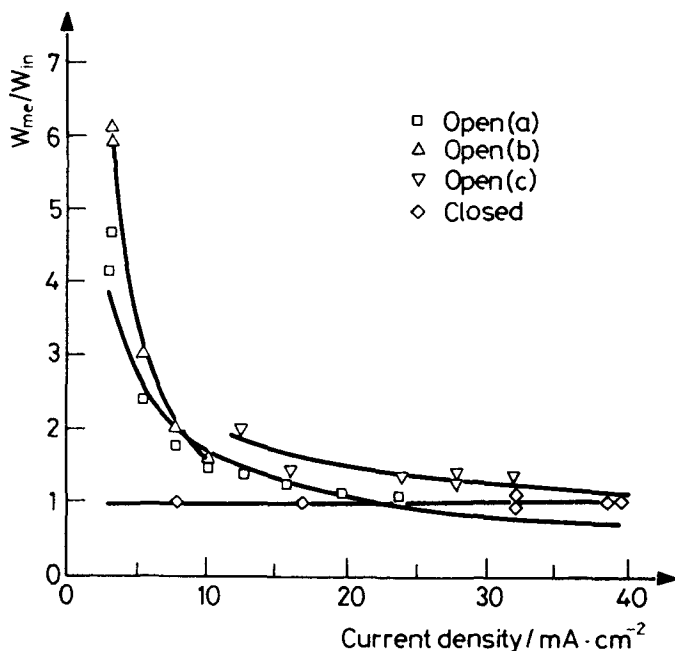


Fig. 4 W_{me}/W_{in} as a function of current density

Table 4 Results of electrolysis of D_2O in open system

I_{in} / mA	$\sigma_{in} / \text{mA} \cdot \text{cm}^{-2}$	E_{cell} / V	W_{me} / mW	W_{in} / mW	$W_{ex.} / \text{mW}$
1.0	1.9	3.41–3.68	2.15– 2.46	1.85– 2.15	0.22 ± 0.15
2.0	3.8	4.00–4.23	5.36– 5.79	4.94– 5.34	0.46 ± 0.08
3.0	5.7	5.67–6.69	16.57–20.86	12.42–15.48	3.72 ± 1.26

W_{me} is a heat measured by calorimeter; $W_{in} = (E_{cell} - E_{th}) \cdot I_{in}$; $W_{ex} = W_{in} - W_{me}$

As we know well, the free-energy change (ΔG) for an overall cell reaction at constant temperature and pressure may be calculated [9] by

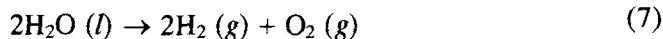
$$\Delta G = -nF(E_c - E_a) = -nFE_{rev} \quad (5)$$

According to the law of thermodynamics, ΔG under the same conditions should be

$$\Delta G = \Delta H - T \Delta S \quad (6a)$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \Delta G = \Delta H^\circ - T\Delta S^\circ + RT \ln Q \quad (6b)$$

For a complete cell reaction of electrolysis process of water, as



Under standard state conditions (1 atm., and 25°C) E_{cc}° is (-1.229) V and (dE_{cc}/dT) is (+0.846) $\text{mV}\cdot\text{K}^{-1}$ and

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \quad \text{or} \quad (8a)$$

$$\Delta H^\circ = -nF [E_{cc}^\circ + T (dE_{cc} / dT)] \quad (8b)$$

Therefore, the E_{th} should be

$$E_{th} = -\Delta H^\circ / nF \quad (9)$$

For the reaction of electrolysis of water, the $E_{th}=1.48$ V.

From the Eqs (3), (5), (6), and (9), the electric work dissipation (W_{el}) during electrolysis should be

$$W_{in} = W_{el} = I (E_{cc} - E_{th}) \quad \text{or} \quad (10a)$$

$$W_{el} = I [T\Delta S^\circ / nF - (RT / nF)\ln Q] + (\eta_a + \eta_c + \eta_{mt} + IR_{cc}) \quad (10b)$$

It is very clear that the Eq. (10) does not represent such a simple linear relationship between the electrical work dissipation and the current density in electrolysis. The reason is that the W_{el} is a nonlinear function of the electrolysis current density according to the right-hand side of the Eq. (10).

Therefore, it may be noted that the W_{in} is equal to W_{el} and the 'excess heat' (W_{ex}) is a nonlinear function of the electrolysis current density. There are many results of calorimetric measurements of the heat generated during an electrolysis of H_2O (or D_2O) [1-6] which can be applied to prove this relationship. This is a preliminary discussion on the heat generated during an electrolysis by general thermodynamics.

Conclusion

This work involved the Calvet type microcalorimeter to search for a low level 'excess heat' generated during electrolysis of water at palladium cathode in the closed and open systems. It is clear that the ratio of heat measured to electric work input in the closed system is almost equal to 1. That ratio is always greater than 1 in the open system. And it varies with electrolysis current density (or voltage).

According to the discussion on the heat generated during electrolysis by general thermodynamics and electrochemistry in this work, it was understood that the 'excess heat' (W_{ex}) should be a nonlinear function of the electrolysis current density.

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Zusammenfassung — Vorliegend werden kalorimetrische Untersuchungen jener Wärme vorgenommen, die bei der Elektrolyse von Wasser unter Anwendung einer Palladiumkathode sowohl in einer normalen offenen als auch einer geschlossenen Zelle beobachtet wird. Für die besagte Wärme wurde ein Unterschied zwischen dem offenen und geschlossenen System festgestellt. Die so unter verschiedenen Bedingungen auftretenden Wärmen wurden als eine Funktion des wirk-samen Stromes oder der Spannung dargestellt. Diese Ergebnisse werden kurz in Bezugnahme auf die allgemeine Thermodynamik und Elektrochemie diskutiert.