Calorimetric investigation of electrochemically induced nuclear fusion of deuterium [a]

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Abstract

Two similar calorimeters electrically connected in series, one for heavy water and the other for ordinary water for comparison, were used in the investigation of their excess heating rates. The production of neutrons, γ-rays, tritium and helium was not investigated in our laboratory. Cathodes for the two calorimeters were made from palladium rods 5.9 mm in diameter and 47 mm in length. They were treated in molten NaOH at 600°C for 1 h to activate their surfaces. Platinum gauze (0.5 mm wire) anodes were used in both calorimeters. For electrolysis, a current of 0.600 A was first maintained for 96 h and was then increased to 0.800 A, 1.000 A and 1.300 A for additional periods of 13 h, 16.5 h and 21 h respectively. A separate measurement with a current of 1.300 A without stirring for 72 h was also made. No evidence of nuclear fusion of deuterium was found in this investigation, which was carried out from 14 April to 16 May, 1989.

Since the claim of Fleischmann and Pons [1] concerning the electrochemically induced nuclear fusion of deuterium on 23 March 1989, heated debates have ensued. The experimental evidence of Fleischmann and Pons included (1) the production of excess heat power, (2) the appearance of neutron radiation and γ-rays, (3) the increase in tritium content, and (4) the formation of helium gas. Various background interferences, however, occurred in the experimental measurements of the last three phenomena. It is therefore hoped that the calorimetric investigation of the excess heat power might give a conclusive answer. Such an investigation would be of value from the practical point of view. However, there are few calorimetric investigations sufficiently quantitative for the purpose. The calorimetric work of Fleischmann and Pons and that of Huggins [2] were not very

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rigorous. For example, their use of the gas bubbles produced for stirring was likely to be insufficient; their determinations of the energy equivalent of the calorimeter and of the Newton's law cooling constant have not been adequately reported; the temperature dependences of these two parameters have apparently not been investigated; and no comparison has been made with experiments on ordinary water. Hence, it seemed to be worthwhile for us to make another investigation.

EXPERIMENTAL

Apparatus

Two identical calorimeters, electrically connected in series, were employed, one for heavy water and the other for ordinary water. One of them is shown in Fig. 1. A glass Dewar vessel with an internal diameter of 4 cm and a depth of 16 cm is closed by a PTFE cover sealed with an O-ring. A ball bearing race at the center of the cover and nickel tubing 3 mm in diameter with a PTFE blade 18 mm in diameter at its lower end form the stirrer for the calorimeter; it is driven by a synchronous motor at 375 rev min^{-1}. Passing through the cover are two tight-fitting glass tubes, one 6 mm in diameter for housing a calibration heater made of insulated constantan wire 0.12 mm in diameter, 300 Ω in resistance, and the other 4 mm in diameter for a thermistor having a resistance of 4 kΩ at 25°C. Both tubes are immersed in silicon oil. The heating voltage and current were measured with two digital voltmeters (error, about 0.3%) once every minute. The heating time was 600 s, counted on a stopwatch.

The temperature of the calorimeter was measured by thermistors. The resistance of one thermistor was measured with an LKB-8700 calorimeter system bridge and that of the other with a QJ49 DC bridge, with the out-of-balance signals monitored on a double-pen strip chart recorder. The thermistors had been calibrated with an HP 2804 quartz thermometer for 10°C increments in the 20–70°C range, and their temperatures were correlated by the relation $R = R_0\, e^{B/T}$, with maximum errors of 0.2 K. The thermal lags were similar to those of the quartz thermometer.

The electrolysis cathode was a palladium rod with surface 5.9 mm in diameter and 50 mm in length activated in molten NaOH at 600°C for 1 h; and its weight was 15.7 g. A platinum wire 0.5 mm in diameter was used as an electrical lead. The palladium rod was fixed between two narrow PTFE plates (see Fig. 1) and had an exposed length of 47 mm. Around the palladium rod were six glass rods 2 mm in diameter, also fixed between PTFE plates, forming a cage. A platinum wire 0.5 mm in diameter and 1600 mm in length wound outside the cage formed the electrolysis anode. The distance between the electrodes was approximately 4 mm. The heater and
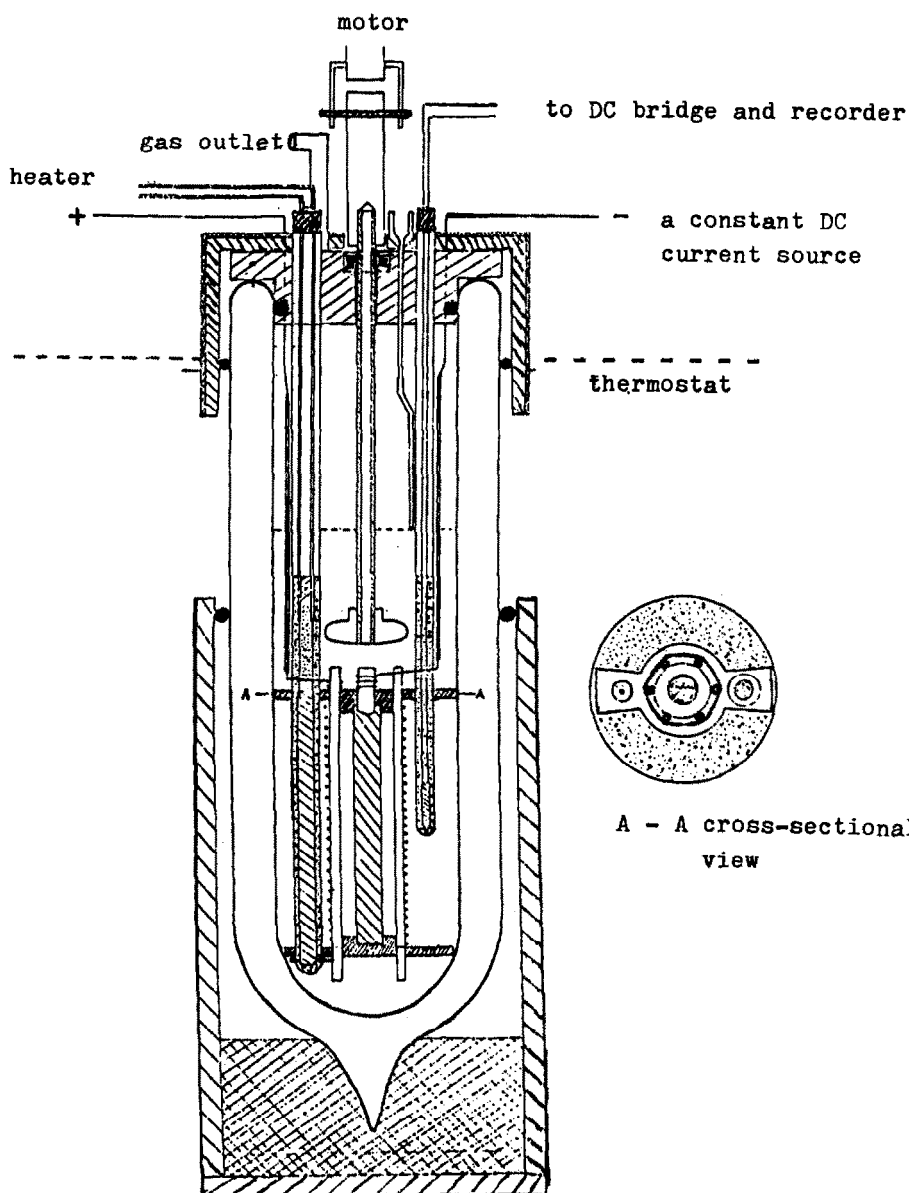
Fig. 1. Schematic diagram of the calorimeter.

the thermistor glass tubes served also as the holders for the entire cage set-up. The electrolyzer diagram is shown in Fig. 2.

On the calorimeter cover was a syringe with PTFE tubing attached to the lower end for addition of heavy or ordinary water to compensate for losses during electrolysis. A soap bubble flowmeter fitted on the gas outlet was used for measuring gas production. Both Dewar vessels were placed in an aluminum cylindrical jacket and immersed in a water thermostat controlled
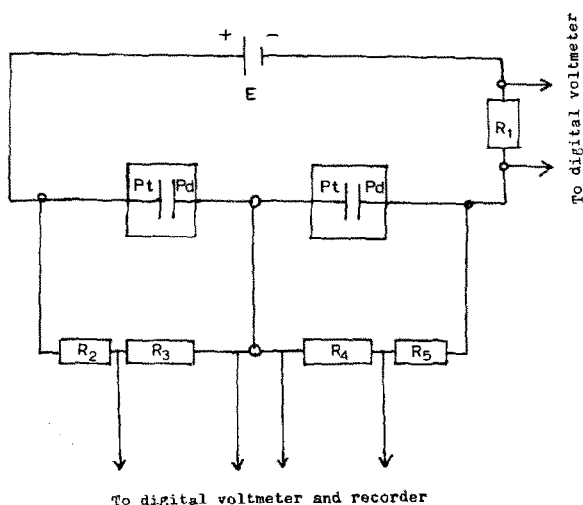
Fig. 2. Electrolyzer diagram: E, YJ-10A adjustable current stabilizer; R_1, 0.1 Ω standard resistor used for calculating the current; R_2 and R_5, 10000 Ω standard resistors; R_3 and R_4, 1000 Ω standard resistors. The voltages across the resistors were measured separately by two digital voltmeters and monitored by two chart recorders.

to $\pm 0.001°$ C. Each of the PTFE calorimeter covers was capped with an aluminum cap 3 mm thick, with its lower part dipping in the water-bath and its top and sides wrapped in three layers of adhesive tape to minimize the influence of fluctuations in room temperature. The ball bearing race of the stirrer was covered with a thin PTFE film and sealed tight with Apiezon to prevent gas leaking through the bearing while allowing the stirrer to rotate.

The calorimeter vessels and all their inner parts were cleaned with distilled water and then with petroleum ether. In calorimeter I was placed 126.0 g of 0.100 M LiOD solution in heavy water (the purity of the heavy water was about 99.9%) and in calorimeter II was placed 121.3 g of 0.100 M LiOH solution in deionized ordinary water. The liquids had a depth of 10.5 cm in the Dewar vessels. The solutions were electrolyzed with two platinum electrodes at 1 A for 20 min to remove any heavy metal ions present. After stopping the electrolysis, the heavy water solution became turbid, with a large number of small bubbles, while the ordinary water solution remained clear, indicating that the heavy water solution has a higher viscosity. Surface tension measurements gave 74.0 dyn cm^{-1} for distilled water, 52.0 dyn cm^{-1} for 0.1 M LiOH in ordinary water and 60.4 dyn cm^{-1} for 0.1 M LiOD in heavy water.

Calibration of the calorimeters

The thermostat was controlled at 40.60° C and the calorimeters were heated to about 37° C. They were calibrated electrically by the usual
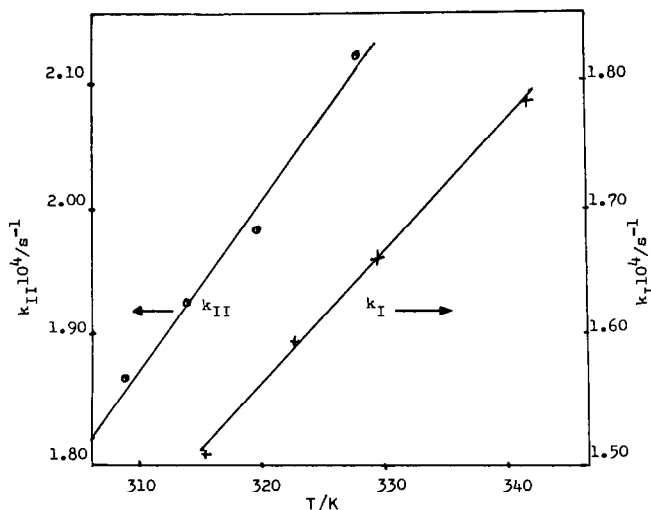
Fig. 3. Temperature dependence of the k value of the calorimeter as determined by using electrical heating.

thermochemical procedure. The temperature rise was $2.662°$ C. For calorimeter I, the energy equivalent E_I was 583 J K^{-1} and the Newton's law cooling constant k_I was 0.000139 s^{-1}. The corresponding values for calorimeter II were $E_{II} = 583$ J K^{-1} and $k_{II} = 0.000188$ s^{-1}.

Since the Newton's law cooling constant k changes with the temperature of the calorimeter system as well as with the temperature difference between the calorimeter and its environment, and since the electrolysis causes a fairly large increase in temperature, it is no longer legitimate to assume that k has the same value in the initial and the final periods as it has in the usual thermochemical procedure. The k values were determined in the following way. After the cessation of electrolysis and a period for completion of the back e.m.f. discharge, the calorimeters were heated electrically with different constant heating powers, W_J, and the equilibrium temperatures of the calorimeter systems were measured. The k values were calculated from the relation $k = W/E\Delta T$, where $W = W_J + W_S$ (the stirring power), ΔT is the difference between the temperature of the calorimeter and that of its environment, and E is their energy equivalent. The k values thus found are plotted in Fig. 3. For comparison, the k values were also estimated from the heating curves for each increase in electrolysis current. The heating curves are represented by the equation

$$T = \left(W/kE + T_j\right) - \left(W/kE + T_j - T_0\right) e^{-kt}$$

where $W = W_J + W_S + W_V$, with W_V referring to the water vaporization, T_0 to the temperature at $t = 0$, T_j is the jacket temperature and t is the time.

TABLE 1

Determined and estimated values of the Newton cooling constant of the calorimeters

k (calorimeter I)				k (calorimeter II)			
T (K)	k [a]	k [b] $(10^4\ s^{-1})$	k [c]	T (K)	k [a]	k [b] $(10^4\ s^{-1})$	k [c]
315.08		1.54	1.48	308.41		1.90	1.76
		(1.51)				(1.83)	
315.19	1.508			308.64	1.867		
322.40	1.596			313.70	1.927		
322.53		1.64	1.57	313.79		1.97	1.90
		(1.60)				(1.93)	
329.12	1.661			319.44	1.983		
330.26		1.74	1.64	319.53		2.06	1.93
		(1.69)				(1.99)	
341.27	1.789			327.51	2.121		
341.91		1.90	1.74	328.32		2.18	2.02
		(1.82)				(2.10)	

[a] k values determined by using constant electrical heating power of the heater to replace the electrolytic heating power, and measuring the equilibrium temperature rise of the calorimeter, and calculated from $k = W/E\Delta T$ with $E = 583$ J K^{-1}.

[b] k values estimated from the cooling curves of the calorimeter.

[c] k values estimated from the heating curves of the calorimeter. The mean of the k values estimated from the heating and cooling curves are given in parentheses.

Similarly, the k values were also estimated from the cooling curves. Because of thermal lag, the k values estimated from the heating curves were lower and those from the cooling curves higher than the values determined from the above experiments. The results are listed in Table 1.

Electrolysis experiments

The thermostat temperature was kept at $25.00 \pm 0.001°$ C. Electrolysis at a current of 0.600 A was maintained for 98 h. The temperature and the voltage reached their steady state values in a few hours. The current was then increased to 0.800 A, 1.000 A and 1.300 A for 13h, 16.5 h and 21 h respectively, followed by electrolysis at 1.300 A for an additional 72 h with no stirring. The equilibrium temperatures and the electrolysis voltages at different currents were measured, the fluctuations in voltage being less than ± 0.01 V. The consumption of water due to electrolysis and evaporation diminished energy equivalents of the calorimeters, and thus caused small drifts in the equilibrium temperature. Warm water was added once a day to keep the calorimeters at their original water level. The temperatures of both calorimeters were thus disturbed and reached equilibrium again after 6 h. Their temperatures were then taken for the calculation of heating power..

TABLE 2

Results of electrolytic experiments [a]

Parameter	Calorimeter							
	I	II	I	II	I	II	I	II
I (A)	0.600	0.600	0.800	0.800	1.000	1.000	1.300	1.300
V (V)	4.037	3.355	4.345	3.702	4.565	3.938	4.983	4.345
W_J (W)	1.498	1.127	2.244	1.777	3.025	2.458	4.476	3.724
W_S (W)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
W_V (W)	−0.018	−0.012	−0.043	−0.022	−0.067	−0.039	−0.186	−0.087
T_{eq} (K)	315.08	308.41	322.28	313.73	330.04	319.42	341.17	328.04
$T_{eq} - T_j$ (K)	16.93	10.26	24.13	15.58	31.89	21.27	43.02	29.89
dv/dt(gas) (ml min^{-1})								
expt.	7.1	7.2					15.5	15.5
calc.	7.0	7.0					15.4	15.4
$k \times 10^4$ (s^{-1})	1.514	1.865	1.575	1.927	1.672	1.982	1.786	2.125
T_{eq}(calc.) (K)	315.03	308.50	322.23	313.86	328.60	319.17	339.45	327.59
ΔT_{eq}(expt. − calc.) (K)	0.05	−0.09	0.05	−0.13	1.44	0.25	1.72	0.45
$\Delta T_{eq}/(T_{eq} - T_j)$ (%)	0.3	−0.9	0.2	−0.8	4.5	1.2	4.0	1.5

[a] Calorimeter I was used for heavy water and calorimeter II for ordinary water. $W_J = (V -$ 1.54$) \times I$ for calorimeter I and $W_S = (V - 1.48) \times I$ for calorimeter II; W_J is the heating power of stirring and W_V the power of water vaporization. T_j is the temperature of the thermostat and is equal to 298.15 K.

EXPERIMENTAL RESULTS

In Table 2 are listed the electrolysis current, voltage, equilibrium temperature, equilibrium temperature rise, the amount of gas produced, Joule heating power due to electrolysis, power needed for water vaporization, and the calculated equilibrium temperature. The theoretical amount of gas production is calculated from the current intensity, and corrections for water vapor pressure and for the temperature of the soap-bubble flowmeter have been made. In the calculation of water vaporization, its gaseous molar volume and the partial vapor pressure at the experimental temperature are considered. The heat of vaporization of water is taken to be 44 kJ mol^{-1}. For calculating the Joule heat, W_J, of electrolysis, 1.54 V (for heavy water) or 1.48 V (for ordinary water) is subtracted from the applied electrolysis voltage. The theoretical temperature rise is equal to $(W_J + W_S + W_V)/kE$ where W_S, the stirring power, is about 0.01 W and W_V is the water vaporization power.

DISCUSSION

(1) From Table 2, the observed equilibrium temperatures and temperature rises of the two calorimeters at different currents agree with the theoretically calculated values. The largest deviation of the temperature rise

is 4.5%, but this is within the uncertainty of our instrumental measurements. The results prove that under our experimental conditions (especially our treatment of the palladium electrode), no excess heat release has been found.

(2) In the calorimetric investigations of Fleischmann and Pons, bubbling of electrolytically produced gases might be insufficient for stirring, especially for heavy water, because of its higher viscosity. In our experiment at 1.3 A, the temperature and the electrolysis voltage increased slightly with no stirring. This might indicate some kind of non-equilibrium. Since our thermometers were placed at fixed locations in our calorimeters, we were unable to measure the temperature distribution in the calorimeter liquid. The temperature of the ordinary water calorimeter changed much less under the same conditions. In our calibration experiments, because we had installed a mechanical stirrer, the rate of temperature change became steady in 25 min after cessation of heating. This indicates that a mechanical stirrer is necessary in electrolysis calorimetry.

(3) In Table 2, it can be seen that the observed gas production and the theoretically calculated value agree with each other. This shows that the current efficiency in the electrolysis is 100% and no recombination reaction of H_2 and O_2 occurred.

(4) Accurate determination of the Newton's law cooling constant k of a calorimeter is very important for the estimation of the heat effect. This constant can be temperature dependent, as was found in our experiment. A reliable method for determining k is to use electrical heating to replace the heating effect of the electrolysis under steady conditions; the k values from cooling or heating curves, especially without stirring, may involve significant errors, and the discrepancy can be serious when the temperature difference between the calorimeter and its environment becomes large. Fleischmann and Pons have not given details for the determination of the k values of their calorimeter which was not mechanically stirred, and therefore their estimation of the excess heating power could be greatly affected.

(5) In our experiment, the heat effects of evaporation and of stirring were estimated and corrected for.

(6) In this work, only the excess heating power has been studied, and a comparison with ordinary water was made. No investigations were undertaken concerning the appearance of neutron radiation and γ rays or the formation of helium gas, as found in Fleischmann and Pons' experiment. Because of the small heating effects, therefore, nothing can be concluded from our experimental investigation.

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