CALORIMETRIC MEASUREMENTS OF THE PALLADIUM/DEUTERIUM SYSTEM: FACT AND FICTION

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The technique, model, and experimental procedures as used in the Fleischmann-Pons calorimetric investigations are described.

I. INTRODUCTION

Following our announcement of the observation of the generation of excess enthalpy in the electrolysis of 0.1 M LiOD solutions in D_2O using palladium cathodes[1] (for some corrections see Ref. 2), there have been numerous comments in the press (and some in the scientific literature[3-14]) about the accuracy of our methods and, therefore, of the validity of our results. It may be of interest to the readership of this journal to compare some of these comments with our actual procedures and results.

Our calorimetric measurements of the palladium/deuterium system in the period leading up to the preliminary publication and subsequently show that it is necessary to make measurements on a large number of electrodes for long times (the mean time chosen for a measurement cycle is 3 months). It is therefore necessary to adopt a low-cost approach; our solution is to use the single-compartment Dewar-cell-type calorimeters illustrated in Fig. 1, and we have maintained up to five of these cells in each of three specially constructed water baths (see Sec. II.C).

II. CRITICISM AND ACTUAL PROCEDURES

We enumerate in this technical note the major criticisms that have been made and compare them to our actual procedures.

II.A. Recombination of Electrogenerated D_2 and O_2 Was Proposed to Occur

It has been suggested that the excess enthalpy observed in our experiments could be due to

1. recombination of D_2 and O_2 generated in the electrolysis on exposed platinum or palladium metal surfaces in the gas head spaces of the cells[15]

2. reduction of anodically generated O_2 (Refs. 4 and 5)

3. oxidation of cathodically generated D_2 (Refs. 4 and 5).

Recombination does not occur because there are no exposed metal surfaces in the gas head spaces (see Fig. 1 and item 1 above) in our cells and because special care has always been taken to ensure that the palladium cathodes and platinum anodes remain totally immersed throughout all of the measurement cycles. Furthermore, the volumes of gas evolved from the cells correspond to that predicted from Faraday's law to better than 99%; in addition, the record of additions of liquid D_2O also match that predicted for a 100%
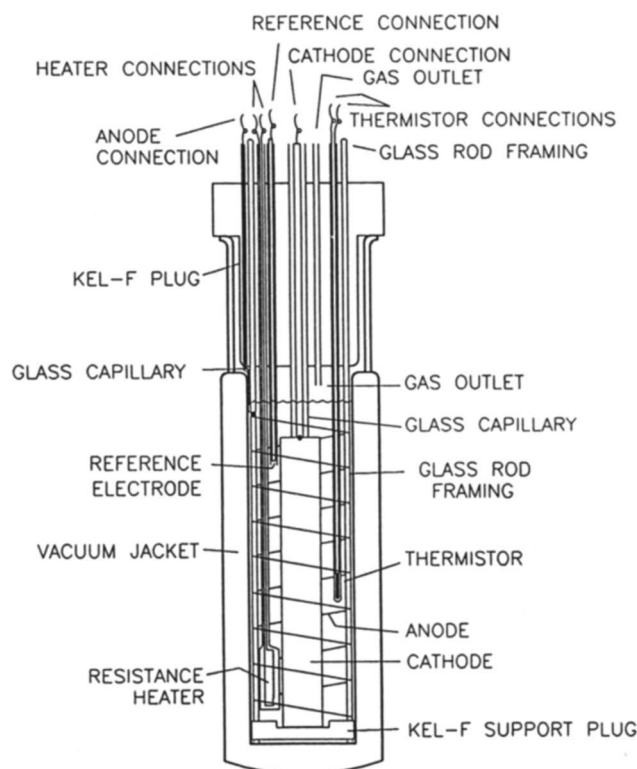

Fig. 1. Single-compartment vacuum Dewar calorimeter cell used in this work.

REFERENCE CONNECTION
CATHODE CONNECTION
HEATER CONNECTIONS
GAS OUTLET
THERMISTOR CONNECTIONS
ANODE CONNECTION
GLASS ROD FRAMING
KEL-F PLUG
GLASS CAPILLARY
GAS OUTLET
GLASS CAPILLARY
REFERENCE ELECTRODE
GLASS ROD FRAMING
VACUUM JACKET
THERMISTOR
ANODE
CATHODE
RESISTANCE HEATER
KEL-F SUPPORT PLUG

efficient Faradaic process (items 2 and 3). This somewhat surprising result, which has also been noted in other work,[16,17] can be understood in terms of the inhibition of D_2 ionization at the anode by platinum oxide formation and by degassing of the electrolyte in the vicinity of the cathode by the rapidly evolving D_2 bubbles. Back reaction of D_2 and O_2 in the cells is also inconsistent with the marked differences between blank experiments and the electrolysis of D_2O using palladium cathodes (see Sec. II.G).

II.B. Analytical Determinations of Gas and Liquid Purity Were Purported to be Absent

The qualitative and quantitative analysis of the gas stream was determined by gas phase chromatography and corroborated the observations reported in Sec. II.A. Isotopic purity of the D_2O solvent was monitored by nuclear magnetic resonance; 99+% purity was observed to hold for all the experiments reported in Refs. 1 and 18.

III.C. Inadequate Mixing of the Electrolyte Leading to Marked Temperature Differences in the Cell

The general principles underlying the design of our calorimeters are outlined elsewhere.[18] We note here that the minimum current used for most of the experiments with rod electrodes was 200 mA. Measurements of the mixing history using dye injection (tracer technique of chemical reaction engineering) showed that radial mixing was extremely rapid even at the minimum gas evolution rate (time scale <3 s). Axial mixing takes appreciably longer ($\cong$20 s), but the axially uniform injection of heat (Fig. 1) ensures that this longer time scale is unimportant because nonuniformities in temperature are equilibrated by radial mixing. As the thermal relaxation time $\tau \cong M^0/4k_R'\theta_{bath}^3$ is $\cong$1600 s (see Sec. II.E and Fig. 4), the calorimeters behave as well-stirred tanks.[19] In agreement with this assessment, measurements of the temperature distribution within the cells (using ensembles of five thermistors that could be displaced radially and axially) showed that the temperature was uniform to within ±0.01°C throughout the bulk of the cells; this variation rose to ±0.02°C in contact with the Kel-F plug at the bottom of the cells. Statements made[3] about large temperature fluctuations in cells of the type used in our experiments were evidently based on measurements using small electrodes in cells constructed from reproductions in newspapers or telecasts of a large device that we have not yet used in our own work. This cell was constructed for work on 2- × 10-cm rod electrodes, which has not yet been initiated.

II.D. Inadequate Control of Water Baths Can Produce Errors

This is of equal importance to the subject of Sec. II.B, and, although this aspect does not appear to have been raised in the literature, we comment on it here as a possible critique of our and other work.

Our water baths are thoroughly insulated (0.5-in.- thick Plexiglas bath surrounded on five sides by 2-in.-thick foam insulation laminated on both sides to aluminum foil, all contained in a reinforced $\frac{1}{16}$-in.-thick steel outer container). The upper surface is allowed to evaporate freely into an atmosphere controlled to ±0.25°C. Use of oversized thermostatting high-velocity circulating pumps ensured that the bath (excluding the top 0.5 cm) was constant to 0.01°C while the fluctuations at any given point were less than ±0.003°C. The water levels in the baths were maintained constant by using

dosimeter pumps connected to additional thermostats. We raise these points to illustrate the care taken to achieve high precision in heat transfer measurements; the control that we achieved may be contrasted to that in other published work, for example, ±0.08°C in Ref. 5, and, indeed, to other operating procedures.[20]

II.E. Incorrect Estimates of the Heat Transfer from the Cell: Random and Systematic Errors

Heat transfer from the cells to the water bath is controlled by a mixture of radiation and conduction (see Nomenclature on p. 677):

$$Q = k_R[(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4] + k_C\Delta\theta . \quad (1)$$

It has been correctly pointed out[5,16] that the use of the linearized form of this equation,

$$Q \cong (4k_R\theta_{bath}^3 + k_C)\Delta\theta , \quad (2)$$

would overestimate Q if $\Delta\theta$ were large. However, the assertion that we use Eq. (2) to make estimates of Q is incorrect. We only use this linearized form of the equation to obtain an algebraic solution of the differential equation representing the "black box" model of the calorimeter (see Sec. II.F) for small values of $\Delta\theta$ in order to assess the validity of the modeling under these conditions (i.e., as a first approximation).

The determination of the heat transfer coefficients requires calibration of the cells, which we carry out by superimposing an additional joule heating term using the electrical heater shown in Fig. 1. This additional heating term ΔQ is applied for 3 h (i.e., >6 thermal relaxation times) with no adjustment to the cell current. In our view, the use of substitution methods (in which the cell current is reduced to compensate for the resistive heating term) leads to unacceptable errors for the following reason: The dissolution of deuterium in palladium is exothermic, and, consequently, any reduction in the cell current leads to a decrease in the concentration of deuterium in the cathode and a resulting cooling of the cathode. It is difficult, if not impossible, to make a quantitative estimate of this effect.

After the establishment of a new thermal equilibrium, we have

$$Q + \Delta Q = k_R[(\theta_{bath} + \Delta\theta + \Delta\Delta\theta)^4 - \theta_{bath}^4]$$
$$+ k_C[\Delta\theta + \Delta\Delta\theta] , \quad (3)$$

and, from Eqs. (1) and (3),

$$\Delta Q = k_R[(\theta_{bath} + \Delta\theta + \Delta\Delta\theta)^4 - (\theta_{bath} + \Delta\theta)^4] + k_C\Delta\Delta\theta . \quad (4)$$

The separate determination of k_R and k_C requires, in effect, the differentiation of data derived from Eq. (4) and therefore leads to an increase in the random errors; furthermore, the accuracy of the determination of Q would in turn depend on the errors in $\Delta\Delta\theta$, which are themselves appreciable (±1%). We have therefore throughout adopted the strategy of neglecting the conductive term while making an appropriate increase in the radiative term

$$Q' \cong k_R'[(\theta_{bath} + \Delta\theta + \Delta\Delta\theta)^4 - (\theta_{bath} + \Delta\theta)^4] , \quad (5)$$

and we thereby obtain an approximate value of Q, Q':

$$Q' \cong \frac{\Delta Q[(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4]}{[(\theta_{bath} + \Delta\theta + \Delta\Delta\theta)^4 - (\theta_{bath} + \Delta\theta)^4]} . \quad (6)$$

We have shown elsewhere[18] that this procedure leads to a *systematic underestimate* of Q (maximally 4%), but the *random* errors are *dramatically* reduced not only because of the avoidance of the separate determination of k_R and k_C but also because the absolute temperatures in Eqs. (5) and (6) are known to much higher precision than are $\Delta\theta$ and $\Delta\Delta\theta$. Since k_R can be estimated from the Stefan-Boltzmann constant $(5.67032 \times 10^{-8}\ \text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4})$ and the radiative area, and k_R' is experimentally determined, the estimate of Q' can be corrected for the neglect of the conductive term by using tabulations of Q'/Q as a function of the magnitude of the conductive contribution to achieve a precision of Q of better than 1% or 1 mW, whichever is the greater. This is the figure that we have always quoted in lectures describing our work. We emphasize that we have always sought to underestimate Q and hence the excess enthalpy.

The procedure embodied in Eqs. (5) and (6) is also important in another regard: Any other term linear in $\Delta\theta$ can be similarly handled by making an appropriate change to k_R [see Sec. II.F comments on Eq. (12)].

Figure 2 illustrates the procedure we followed to make preliminary estimates of k_R' and Q'. We emphasize that we have never made an estimate of Q without carrying out a calibration cycle.

II.F. Incorrect Estimates of the Heat Transfer from the Cell: The "Black Box" Model

The "black box" model of the calorimeter is represented in Fig. 3a; the nature of most of the enthalpy terms is readily apparent. We note here the following points:

1. The enthalpy input to the cell is $[E_{cell}(t) - \gamma E_{thermoneutral,cell}]I$, where $E_{thermoneutral,cell}$ is the cell potential at which the cell neither absorbs nor gives off heat. This differs from the reversible potential for the cell reaction

$$2D_2O \rightleftharpoons 2D_2 + O_2$$
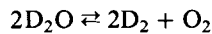
since the reaction proceeds with an increase of entropy. The current efficiency γ is close to unity (see Sec. II.A).

2. The enthalpy of the gas stream includes the term

$$\frac{\gamma I}{F}\left[0.75\left(\frac{P}{P^* - P}\right)C_{P,D_2O,v}\Delta\theta + 0.75\left(\frac{P}{P^* - P}\right)L\right]\ ,$$

due to the evaporation of D_2O to saturate the gas stream and the heating of this component of the gas stream to the cell temperature. We have neglected this term and this leads to an underestimate of Q and hence of Q_f. When the temperature of the cell approaches the boiling point, the latent heat of evaporation becomes the dominant heat transfer term. The calorimeters are unsuitable for making measurements under such conditions.

3. For a continuously reacting chemical system (open system) such as that in the electrochemical Dewar cells, the cell contents change with time. Consequently, the heat transfer coefficients are time dependent, and this also affects the heavy water equivalent of the cell (see item 5 below). The extent of the radiant surface decreases with time while the length of any parallel conduction path increases with time. To a close approximation, we therefore expect the heat transfer coefficients to decrease linearly with time. For example, using the approximation outlined in Sec. II.E, we have
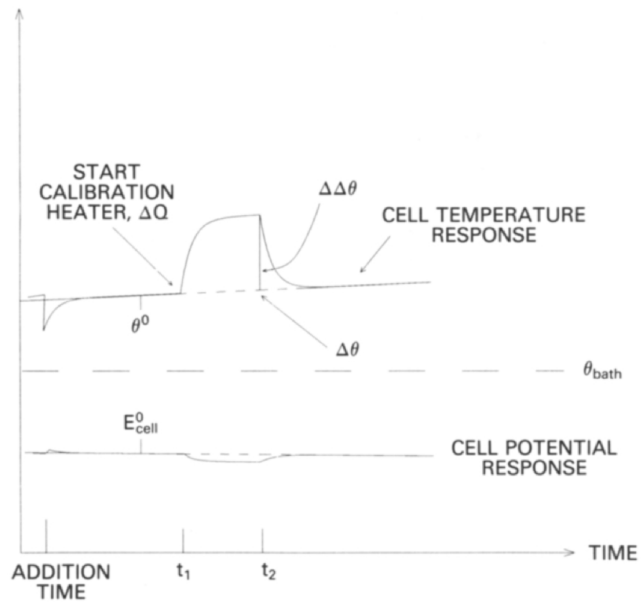

Fig. 2. Schematic for the experimental determination of approximate heat flow in the calorimeter. The response shows the application of the calibration pulse of strength ΔQ, which leads to an eventual new sloping steady-state temperature $\Delta\Delta\theta\ °C$ above the linearly sloping baseline temperature. Calculation of the output heat flow at this level of approximation requires simply the measurement of the three temperatures indicated and the magnitude (ΔQ) of the calibration heater pulse. In applying Eq. (13), it is convenient to set the origin $t = 0$ at ≈ 6 thermal relaxation times following the addition of D_2O to make up for losses due to electrolysis and evaporation. At this point $\theta = \theta^0$, $E_{cell} = E_{cell}^0$, $k_R' = k_R'^0$, and $M = M^0$.

$$k_R'^0\left[1 - \frac{(1 + \lambda)\gamma It}{2FM^0}\right][(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4]\ ,\qquad(7)$$

where the term λ allows for a more rapid decrease of the radiant surface area and increase of the length of the conduction path than would be predicted by electrolysis alone in view of the effects of the internal solid components (glass rods, tubes). The superscript 0 here (and elsewhere) denotes a value at a chosen time origin.

4. The effects of the addition of D_2O to make up for electrolysis (and evaporation at higher temperatures) can be neglected, provided evaluations are started following the elapse of at least six thermal relaxation times.

5. In the general differential of the water equivalent

$$M = M^0 - \frac{(1 + \beta)\gamma It}{2F}\ ,\qquad(8)$$

the term β allows for a more rapid decrease of M than would be predicted by electrolysis and evaporation alone. We expect β to be small compared to λ.

6. Using the enthalpy balance defined by the "black box" (Fig. 3a), we obtain the differential equation governing the θ-t dependence:

ENTHALPY OF GAS STREAM

$$\gamma \frac{I}{F} \left\{ \left[0.5C_{P,D_2} + 0.25C_{P,O_2} + 0.75 \left(\frac{P}{P^* - P} \right) C_{P,D_2O,v} \right] \Delta\theta + 0.75 \left(\frac{P}{P^* - P} \right) L \right\}$$

$[E_{cell}(t) - \gamma E_{thermoneutral,cell}] I \longrightarrow$

ENTHALPY INPUT TO THE CELL

$$C_{P,D_2O,l} \left[M^0 - (1+\beta)\frac{\gamma I t}{2F} \right] \frac{d\Delta\theta}{dt}$$
$$- (1+\beta)\frac{\gamma I}{2F} C_{P,D_2O,l} \Delta\theta$$

$\longrightarrow$ RADIATION AND CONDUCTION

HEAT LOSS FROM THE CELL

EXCESS ENTHALPY

Q_f

CALIBRATION PULSE

$+\Delta QH(t - t_1)$
$-\Delta QH(t - t_2)$

$$\gamma \frac{I}{F} \int_0^t \left[0.5 + 0.75 \frac{P}{P^* - P} \right] C_{P,D_2O,l} \Delta\theta' \, dt$$

ENTHALPY OF MAKE-UP STREAM

(a)

$[E_{cell}(t) - E_{thermoneutral,bath}] I \longrightarrow$

$$C_{P,D_2O,l} \left[M^0 - (1+\beta)\frac{I t}{2F} \right] \frac{d\Delta\theta}{dt}$$
$$- \frac{\beta I}{2F} C_{P,D_2O,l} \Delta\theta$$

$\longrightarrow$ RADIATION AND CONDUCTION

Q_f
$+\Delta QH(t - t_1)$
$-\Delta QH(t - t_2)$

$$\frac{I}{F} \int_0^t \left[0.5 + 0.75 \frac{P}{P^* - P} \right] C_{P,D_2O,l} \Delta\theta' \, dt$$
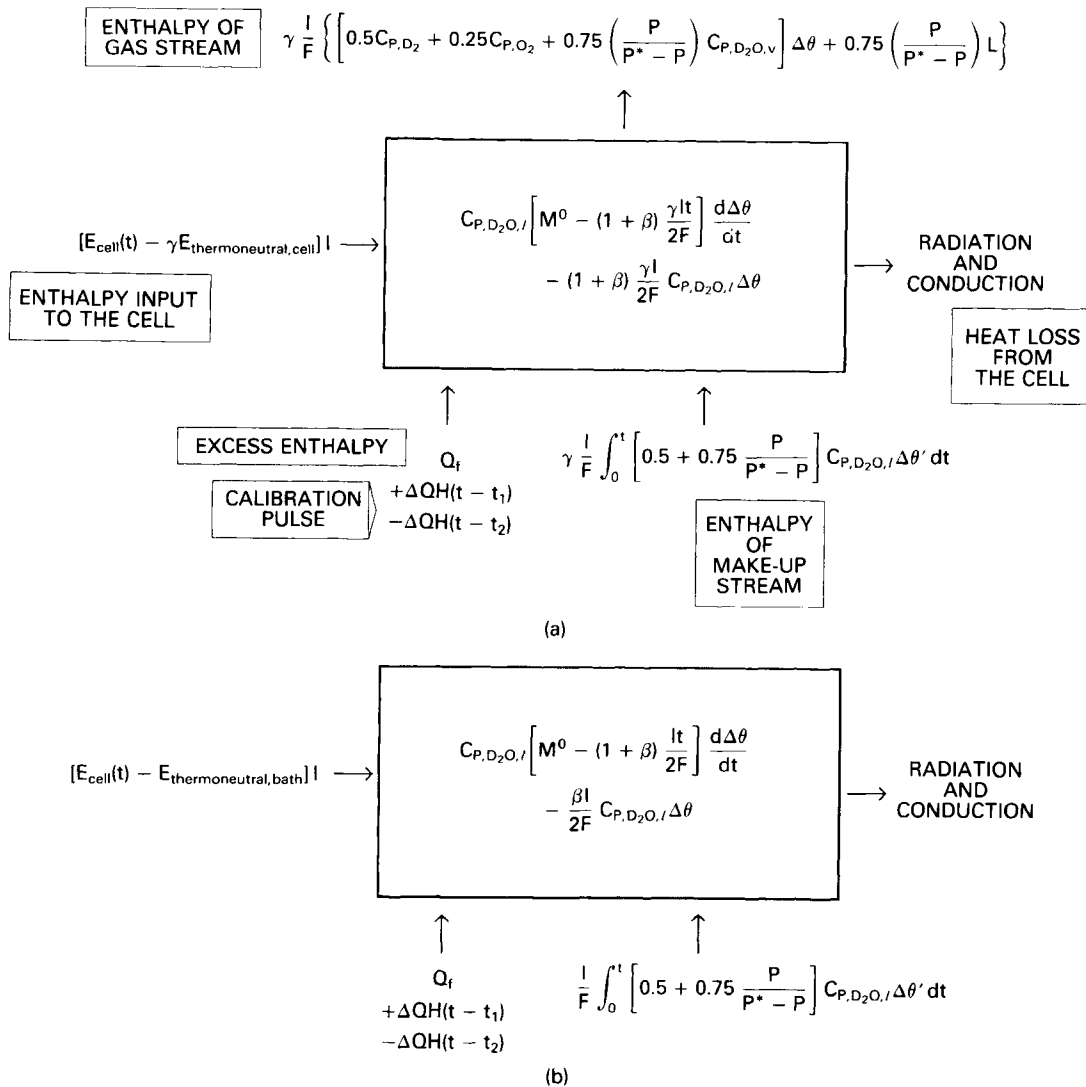
(b)

Fig. 3. (a) Schematic of the complete "black box" used for modeling the Dewar calorimeter shown in Fig. 1 and (b) the actual model used for determining the heat flow in the cell and considering that $\gamma \cong 1$.

$$C_{P,D_2O,l} \left[M^0 - \frac{(1+\beta)\gamma I t}{2F} \right] \frac{d\Delta\theta}{dt} - C_{P,D_2O,l} \frac{(1+\beta)\gamma I \Delta\theta}{2F}$$

$$= [E_{cell}(t) - \gamma E_{thermoneutral,cell}] I + Q_f(t)$$

$$+ \Delta QH(t - t_1) - \Delta QH(t - t_2)$$

$$- \frac{\gamma I}{F} \left\{ \left[0.5C_{P,D_2} + 0.25C_{P,O_2} + 0.75 \left(\frac{P}{P^* - P} \right) \right. \right.$$

$$\left. \times C_{P,D_2O,v} \right] \Delta\theta + 0.75 \left(\frac{P}{P^* - P} \right) L \right\}$$

$$- k_R'^0 \left[1 - \frac{(1+\lambda)\gamma I t}{2FM^0} \right] [(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4] \ .$$

$$(9)$$

With the relation

$$\Delta H_{cell}^\varnothing = \Delta H_{bath}^\varnothing + \sum_i \nu_i C_{P,i} \Delta\theta \ , \tag{10}$$

the "black box" (Fig. 3a) simplifies to that shown in Fig. 3b. Here we also take into account item 2 and that the current efficiency $\gamma \cong 1$. We obtain the modified differential equation governing the behavior of the calorimeter:

$$C_{P,D_2O,l} \left[M^0 - \frac{(1+\beta)I t}{2F} \right] \frac{d\Delta\theta}{dt} - C_{P,D_2O,l} \frac{\beta I \Delta\theta}{2F}$$

$$= [E_{cell}(t) - E_{thermoneutral,bath}] I$$

$$+ Q_f(t) + \Delta QH(t - t_1) - \Delta QH(t - t_2)$$

$$- k_R'^0 \left[1 - \frac{(1+\lambda)I t}{2FM^0} \right] [(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4] \ . \tag{11}$$

7. Equation (11) is difficult to apply since $E_{cell}(t)$ and $Q_f(t)$ are unknown functions of time. However, we note that the overpotentials and the conductance can all be expressed by Taylor series expansions about a chosen origin in temperature θ^0. Since the variations in temperature are small

in any given measurement cycle, we are only concerned with first derivatives and obtain

$$\left(\frac{dE_{cell}}{d\theta}\right)I\Delta\theta' = \frac{\psi I}{\theta^0}\,\Delta\theta' \ . \tag{12}$$

The magnitude and even the sign of ψ are difficult to predict, so that it is best to derive this as an empirical constant from the experimental observations. This procedure also has the advantage that it automatically corrects for other unquantified changes in the enthalpy input, e.g., those due to changes in the concentration of the electrolyte. We can therefore cast Eq. (10) into the tractable form

$$C_{P,D_2O,l}\left[M^0 - \frac{(1+\beta)It}{2F}\right]\frac{d\Delta\theta}{dt} - C_{P,D_2O,l}\frac{\beta I\Delta\theta}{2F}$$

$$= \left(E_{cell}^0 - E_{thermoneutral,cell} + \frac{\psi\Delta\theta'}{\theta^0}\right)I + Q_f(t)$$

$$+ \Delta QH(t - t_1) - \Delta QH(t - t_2)$$

$$- k_R'^0\left[1 - \frac{(1+\lambda)It}{2FM^0}\right][(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4] \ . \tag{13}$$

8. We assume $Q_f(t)$ to be constant during any one measurement cycle.

9. The algebraic solution of Eq. (13) [using the linear form Eq. (2) in place of the quadratic term in Eq. (13)] shows that the appropriate heat transfer coefficient is

$$\left(4k_R^0\theta_{bath}^3 + k_C^0 - \frac{\psi I}{\theta^0}\right)\left[1 - \frac{(1+\lambda)It}{2FM^0}\right]$$

rather than the form

$$(k_R^0\theta_{bath}^3 + k_C^0)\left[1 - \frac{(1+\lambda)It}{2FM^0}\right] \ ,$$

which would be predicted from the heat balance at a single point.[18] This would indeed be expected from the argument outlined in Sec. II.E. The algebraic solution closely fits the experimental data for small values of $\Delta\theta$. More generally and for higher accuracy, we must fit the whole transient predicted from the inhomogeneous nonlinear differential equation [Eq. (13)] to the experimental data set. We use the simplest forward integration procedure

$$\Delta\theta_{n+1,calc} = \Delta\theta_{n,calc} + \left(\frac{d\Delta\theta_{calc}}{dt}\right)_n\Delta t \ , \tag{14}$$

and in forming

$$\chi^2 = \sum_{n=1}^{N}\frac{(\Delta\theta_{n,exp} - \Delta\theta_{n,calc})^2}{\sigma_n^2} \ , \tag{15}$$

we take the standard deviation as

$$\sigma_n^2 = \frac{10^{-4}}{(\Delta\theta_{n,exp})^2} \ . \tag{16}$$

We have left all parameters free in the fitting procedure. The curvatures of the hyperspaces along the axes

$$\frac{(E_{cell,t=0} - E_{thermoneutral,bath})I + Q_f}{C_{P,D_2O,l}}$$

and M^0 in the parameter space are similar, so a minimization using these free parameters converges badly. We therefore find it convenient to define one independent parameter as

$$\frac{(E_{cell,t=0} - E_{thermoneutral,bath})I + Q_f}{C_{P,D_2O,l}M^0} \ . \tag{17}$$

Furthermore, we also find it convenient (though not essential) to derive the value of the parameter

$$\frac{\psi I}{C_{P,D_2O,l}M^0\theta^0} \tag{18}$$

by first fitting data of E_{cell} versus $\Delta\theta$ using linear regression. By using Eq. (18), the optimization is reduced to four parameters and, by also using Eq. (17) the sensitivity of the calculation to M^0 is greatly increased, thereby speeding the calculation.[18]

We have used a Marquardt-type algorithm[21] throughout this work in which the diagonal elements of the matrix equation derived from the minimization procedure are scaled appropriately so as to follow either a path of steepest descent or along the directions of the parameter space as required to optimize the reduction of χ^2. The calculation is carried out iteratively until both the parameters and χ^2 have converged adequately.

The procedure outlined above has two particular advantages compared to other methods of data evaluation. First, the entire experimental data set (typically 1000 data points including the highly structured region due to the application and removal of the resistive heating term ΔQ) is used to derive the four key parameters. Second, the variances of the parameters are given to a close approximation by the diagonal elements of the inverse of the error matrix. We cannot stress the importance of this point too highly: In carrying out experiments on novel systems, the standard deviation of any derived parameter must be derived from each individual experiment, not from a set of derived parameters because the variability of the experiment may be an inherent feature of the system.

In carrying out the calculation, we used the parameters obtained as outlined in Sec. II.E as starting values as they are already close to the "best" values. We are naturally mostly interested in the parameter (17), which we found can be calculated to ±0.1% by this procedure. As the error in M^0 is very small ($\cong$0.01%), the error in the total output enthalpy is approximately equal to ±0.1%, which is in the range 0.1 to 10 mW in our experiments. Note that even higher precision could be obtained by using a larger number of calibration pulses, but we have not developed such measurements since the error in Q_f is increased over that of the total output enthalpy by the error in Q_{input}, which in our experiments has been dominated by the term $Q_{input}\Delta I/I$ (we note $\Delta I/I \cong$ 0.1% at all current densities). This error is again in the range 0.1 to 10 mW, depending on the current density and electrode dimension.

Figure 4 illustrates the degree of fit between the experimental and derived θ-t profiles that can be obtained in following the methodology outlined in this section. Table I lists some of the results obtained to date for the palladium/D_2O system.

II.G. Absence of Blank Experiments

We believe that the allegations in *Nature*[22] that we had not carried out blank experiments before the publication of our preliminary note[1] have been one of the principal factors
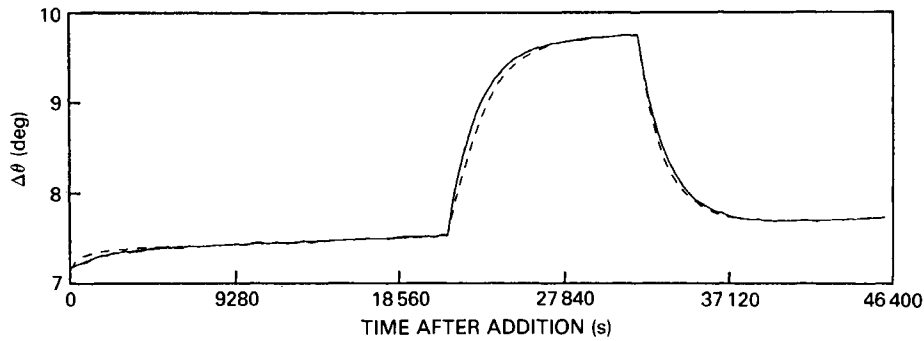
Fig. 4. The degree of fit of the "black box" model in Fig. 3b to actual experimental data from an experiment using a 0.2- × 10-cm palladium rod cathode in 0.1 M LiOD. The broken line represents the fit obtained using estimated values of the several cell parameters and was obtained by the forward integration technique described in the text to force the fit of the data to the model at the starting point ($t = 0$), the point of application of the calibration heater pulse, the point at the end of the calibration heater pulse, and the point at the end of the experiment. The solid line (which in this figure is coincident with the experimental data) is the fit obtained to the model by the Marquardt algorithm for the nonlinear regression technique described in the text.

TABLE I

Excess Enthalpy Observed for 0.1-, 0.2-, and 0.4-cm-diam Palladium Rods as a
Function of Current Density and Electrolyte Composition

Rod Diameter[a] (cm)	Electrolyte[b]	Current Density (mA·cm^{-2})	E_{cell} (V)	Q_{input} (W)	Q_{excess} (W)	Approximate Specific Q_{excess} (W·cm^{-3})	Specific Q_{excess} from Regression Analysis (W·cm^{-3})
0.1	$\mathfrak{D}$	64	3.637	0.419	0.042	0.53	0.581 ± 0.003
0.1*	$\mathfrak{J}$	64	2.811	0.032	0.001	0.140	0.1442 ± 0.0002
0.1	$\mathfrak{D}$	128	4.000	0.984	0.160	2.04	2.043 ± 0.003
0.1*	$\mathfrak{J}$	128	3.325	0.089	0.005	0.486	0.5131 ± 0.0006
0.1	$\mathfrak{D}$	256	5.201	2.93	0.313	3.99	4.078 ± 0.007
0.1*	$\mathfrak{D}$	512	9.08	1.51	0.17	17.3	18.19 ± 0.02
0.1	$\mathfrak{D}$	512	6.085	7.27	1.05	13.4	13.77 ± 0.02
0.1*	$\mathfrak{D}$	1024	11.640	4.04	1.03	105	112.8 ± 0.1
0.2	$\mathfrak{D}$	64	4.139	1.040	0.123	0.39	0.419 ± 0.003
0.2	$\mathfrak{J}$	64	4.780	1.30	0.006	0.019	0.021 ± 0.001
0.2	$\mathfrak{M}$	64	3.930	0.956	0.024	0.077	0.077 ± 0.001
0.2	$\mathfrak{D}$	128	8.438	5.52	1.65	5.25	5.68 ± 0.01
0.2*	$\mathfrak{J}$	128	4.044	0.250	0.028	0.713	0.714 ± 0.001
0.2*	$\mathfrak{M}$	256	6.032	0.898	0.056	1.42	1.498 ± 0.002
0.2*	$\mathfrak{D}$	512	8.25	2.68	0.66	16.8	17.02 ± 0.04
0.2*	$\mathfrak{M}$	512	9.042	3.00	0.603	15.3	16.03 ± 0.01
0.2*	$\mathfrak{J}$	1024	7.953	5.13	2.80	71.2	75.42 ± 0.08
0.4	$\mathfrak{D}$	64	5.137	2.88	0.502	0.40	0.411 ± 0.001
0.4	$\mathfrak{D}$	64	5.419	3.10	0.263	0.209	0.214 ± 0.003
0.4**	$\mathfrak{D}$	64	4.745	2.24	0.117	0.106	0.145 ± 0.002
0.4*	$\mathfrak{M}$	64	3.519	0.198	0.0005	0.002	0.0023 ± 0.0002
0.4	$\mathfrak{D}$	128	6.852	8.50	1.05	0.84	0.842 ± 0.009
0.4*	$\mathfrak{D}$	256	7.502	2.38	0.311	1.98	1.999 ± 0.003
0.4*	$\mathfrak{D}$	512	8.66	5.70	2.18	13.9	14.41 ± 0.05
0.4*	$\mathfrak{D}$	512	10.580	7.23	1.65	10.5	11.09 ± 0.02

[a]All rod lengths are 10, 1.25*, or 8.75** cm.
[b]$\mathfrak{D}$ = 0.1 M LiOD; $\mathfrak{J}$ = 0.50 M Li$_2$SO$_4$; $\mathfrak{M}$ = 0.1 M LiOD + 0.45 M Li$_2$SO$_4$. All measurements were made in the same batch of D$_2$O of 99.9% isotopic purity. Measurements using electrolytes labeled $\mathfrak{J}$ and $\mathfrak{M}$ were made after March 23, 1989.

in preventing a logical development of research in this area and in polarizing attitudes. These allegations are difficult to understand since the preliminary publication did in fact contain one blank experiment (sheet electrode at low current density), which gave an exact enthalpy balance with $Q_f = 0$. Our view has always been that a palladium electrode that does not show excess enthalpy in D_2O is the most appropriate blank.

Table II gives an extensive list of blank experiments. Many of these were available at the time of our first preliminary publication.[1] The excess enthalpies are all slightly negative, which can be understood in terms of the comments in Sec. II.E: The inclusion of the linear conductance term in the quadratic radiative term by adjusting the radiative heat transfer coefficient leads to a systematic underestimate of the heat output in the cell and hence a negative "excess" enthalpy.

We regard the essentially zero excess enthalpy observed on 0.8-cm-diam palladium electrodes in D_2O as the most significant blank; it is untrue, as has frequently been stated,[23] that we have not carried out experiments on the palladium/D_2O system showing zero excess enthalpy. Excess heat generation on 0.8-cm-diam electrodes has only recently been observed by us using a new batch of electrodes prepared by modified procedures.

III. DISCUSSION

It can be seen that most of the speculations that have been published about our experimental procedures and results are exaggerated at least. In particular, it is perfectly feasible to derive very accurate values of the heat output from the simple Dewar-type cells, provided adequate precautions are taken in the experiment design and modern methods of data analysis are used. We believe that more accurate values of the heat outputs could not be derived by using more complex instrumentation. A further consequence follows from the simplicity of the design (Fig. 1). It is relatively straightforward and inexpensive to scale the cells so that the measured excess enthalpies become large compared to the random errors.

The marked excess enthalpies (Table I) must be viewed in terms of the small negative excesses for the blank experiments (Table II). The increase in the excess enthalpy with current density is very marked and at least of the order I^2 with no indication of a limit at the highest current density used ($1 A \cdot cm^{-2}$). At this current density the excess enthalpy reaches $100 W \cdot cm^{-3}$, in agreement with another recent report.[24] The marked increase in the excess enthalpy with current density gives the results the appearance of a threshold phenomenon, but further measurements of very high accuracy at low current densities are needed to clarify this question. The scatter in the results at intermediate current densities is very large compared to the experimental errors, and this scatter may well be due to the approach to a threshold. The variability in this region may also explain some of the diversity in the reported results since such intermediate current densities have been extensively used by other investigators.

In addition to the baseline excess enthalpies such as those

TABLE II

Results for Blank Experiments on Platinum and Palladium Rods as a
Function of Current Density and Electrolyte Composition

Rod Diameter[a] (cm)	Electrolyte[b]	Current Density (mA·cm^{-2})	E_{cell} (V)	Q_{input} (W)	Q_{excess} (W)	Approximate Specific Q_{excess} (W·cm^{-3})	Specific Q_{excess} from Regression Analysis (W·cm^{-3})
Palladium Electrodes							
0.1	𝔚	32	3.605	0.212	−0.001	−0.009	−0.0097 ± 0.0002
0.1	𝔚	64	3.873	0.479	−0.001	−0.014	−0.0165 ± 0.0005
0.1[c]	𝔚	128	5.186	1.482	−0.001	−0.001	
0.1[c]	𝔚	256	8.894	5.931	−0.001	−0.007	
0.1	𝔚	512	11.29	15.70	−0.001	−0.008	−0.01 ± 0.02
c,d	𝔇	0.8	2.604	1.458	−0.001	−0.000	
0.8[c]	𝔇	8	3.365	0.365	−0.001	−0.000	
0.8[c]	𝔇	8	3.527	0.397	−0.003	−0.000	
Platinum Electrodes							
0.1[c]	𝔇	64	3.800	0.452	0.000	0.000	
0.1[c]	𝔇	64	4.138	0.520	−0.001	−0.008	
0.1[c]	𝔇	256	6.218	3.742	−0.001	−0.028	
0.1	𝔚	64	4.602	0.624	−0.002	−0.023	−0.0232 ± 0.0006
0.1	𝔚	64	4.821	0.668	−0.003	−0.038	−0.0392 ± 0.0006
0.1	𝔚	512	12.02	16.86	−0.001	−0.007	−0.01 ± 0.02

[a]All rod lengths are 10 cm.
[b]𝔇 = 0.1 M LiOD; 𝔚 = 0.1 M LiOH; all measurements in D_2O were made in the same batch as used in the experiments in Table I.
[c]Data available March 23, 1989. These data were evaluated by another method and not by those described in this technical note.
[d]Palladium sheet electrode = 8 × 8 × 0.2 cm.

given in Table I, we have observed "bursts" in the excess enthalpy production,[18,19] which have now also been observed by a number of other research groups.[17,25-28] The most prolonged burst that we have recorded to date is illustrated in Fig. 5a. The excess specific enthalpy is given in Fig. 5b, and the cumulative excess specific enthalpy in Fig. 5c. It is not clear at the present time whether the baseline production of excess enthalpy and the bursts are in any way causally linked or whether the generation of excess enthalpy is linked to the production of tritium or neutrons. It is certainly true that the tritium levels increase markedly following a burst (factors of 8 have been observed in the National Cold Fusion Institute laboratories[29]), but these increases are insignificant compared to the heat produced, if we assume the "normal" tritium output channel is responsible.

The rates of enthalpy production during the bursts are 17 times (plateau levels) and 40 times (peak values) of the total enthalpy input to the cells. The cumulative excess enthalpy for the bursts shown in Figs. 5a, 5b, and 5c ≈ 16 MJ$\cdot$cm^{-3} far exceeds the heat that could be generated by any conceivable chemical process (factor of 10^2 to 10^3). This is equally true of the baseline excess enthalpies generated over the experimental durations (typically ≈ 50 MJ$\cdot$cm^{-3}). We fail to see how such large specific enthalpies could be attributed to anything other than a nuclear process (cf. Ref. 30; "Wigner"-type energy releases, which have also been suggested as a cause for the observation of anomalous energy releases,[31] would also be much too small to account for the observed effects).

We note that the use of energy-efficient systems (D_2 ionization at the anode, small interelectrode gaps, high electrolyte concentrations) would give energy-producing systems
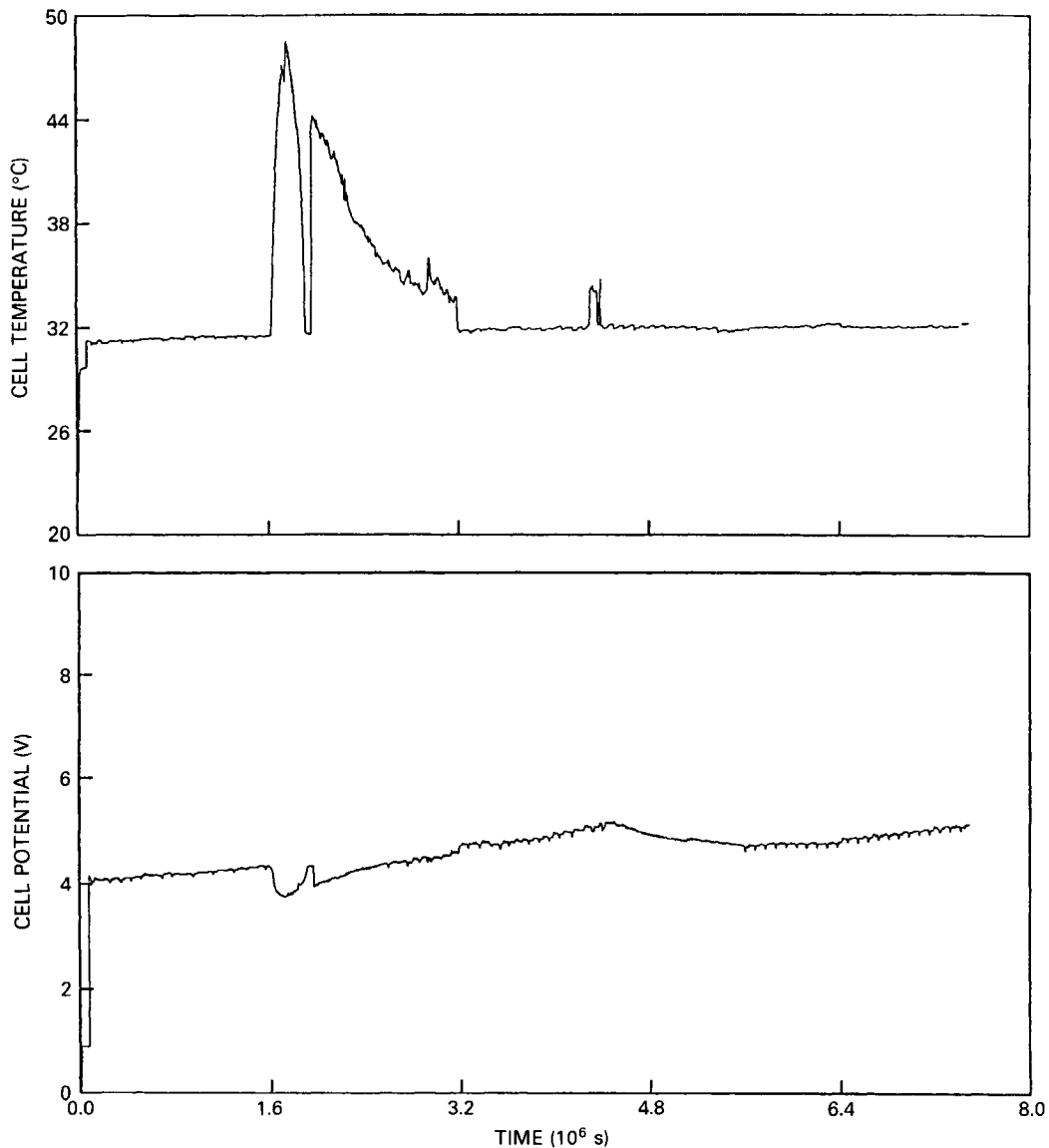

Fig. 5a. Demonstration of a burst of excess enthalpy for a long period of time. The figure shows the cell temperature versus time (upper plot) and the cell potential versus time (lower plot) for a 0.4- × 1.25-cm palladium rod electrode in 0.1 M LiOD solution. The current density was 64 mA$\cdot$ cm^{-2}, and the bath temperature was 29.87°C.
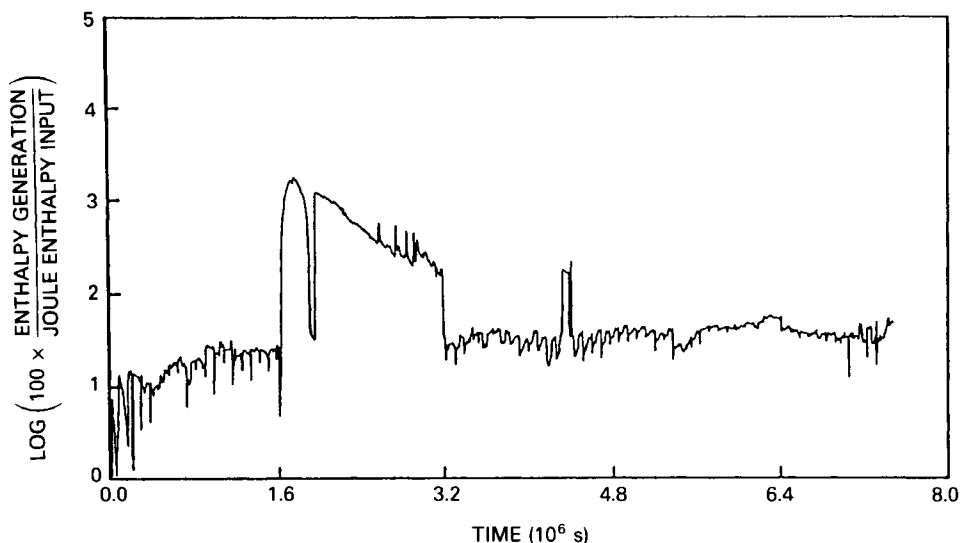
Fig. 5b. The calculated rate of excess enthalpy generation as a function of time.
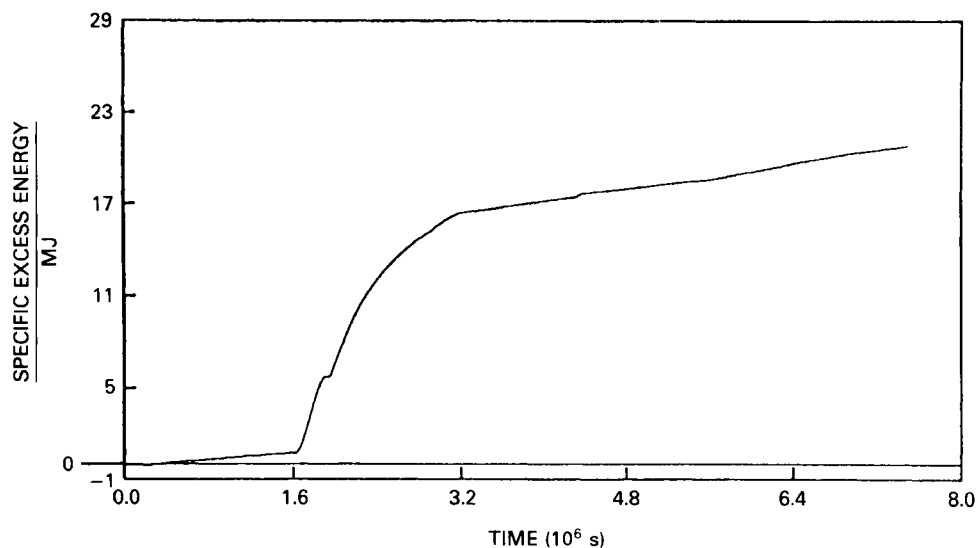

Fig. 5c. The total specific excess energy output as a function of time for this cell.

even for some of the baseline excess enthalpies already reported. During bursts the system we have described is an effective energy producer even in its present inefficient form (oxygen evolution at the anode, relatively large anode-cathode spacing, low conductivity electrolyte).

NOMENCLATURE

$C_{P,D_2O,l}$ = heat capacity of liquid D_2O $(J \cdot K^{-1} \cdot mol^{-1})$

$C_{P,D_2O,v}$ = heat capacity of D_2O vapor $(J \cdot K^{-1} \cdot mol^{-1})$

$C_{P,i}$ = heat capacity of O_2, D_2, or $(D_2O)_l$ $(J \cdot K^{-1} \cdot mol^{-1})$

E_{cell} = measured cell potential (V)

$E_{cell,t=0}$ = measured cell potential at the time when the initial values of the parameters are evaluated (V)

$E_{thermoneutral,bath}$
= potential equivalent of the enthalpy of reaction for the dissociation of heavy water at the bath temperature (V)

F = Faraday constant $(96484.56°C \cdot mol^{-1})$

H = Heaviside unity function

I = cell current (A)

k_C = heat transfer coefficient due to conduction $(W \cdot K^{-1})$

k_R = heat transfer coefficient due to radiation $(W \cdot K^{-4})$

$k_R^{\prime 0}$ = effective heat transfer coefficient due to radiation at a chosen time origin $(W \cdot K^{-4})$

k_R'	= effective heat transfer coefficient due to radiation $(W \cdot K^{-4})$
$k_R'^0$	= effective heat transfer coefficient due to radiation at a chosen time origin $(W \cdot K^{-4})$
l	= liquid phase
L	= enthalpy of evaporation $(J \cdot mol^{-1})$
M	= heavy water equivalent of the calorimeter (mol)
M^0	= heavy water equivalent of the calorimeter at a chosen time origin (mol)
n	= iteration number (data point number)
P	= partial pressure (Pa)
P^*	= atmospheric pressure (Pa)
Q	= rate of steady-state heat generation at a given temperature (W)
Q_f	= rate of generation of excess enthalpy (W)
t	= time (s)

Greek

β	= dimensionless term allowing for more rapid time-dependent decrease of water equivalent of cell than that expected from electrolysis alone
γ	= current efficiency of electrolysis toward a given reaction
$\Delta H^{\varnothing}$	= standard free enthalpy change $(J \cdot mol^{-1})$
ΔQ	= rate of heat dissipation of calibration heater (W)
$\Delta \theta$	= difference in cell and bath temperature at a given rate of enthalpy release (K)
$\Delta \theta'$	= $\Delta \theta - \Delta \theta^0$ (K)
$\Delta \theta^0$	= difference in temperature between the cell and the bath at a chosen time origin (K)
$\Delta \theta_n$	= difference in cell and bath temperature at the n'th time interval (K)
$\Delta \theta_{n,calc}$	= calculated difference in cell and bath temperature at the n'th time interval (K)
$\Delta \theta_{n,exp}$	= difference in experimental cell and bath temperature at the n'th time interval (K)
$\Delta \Delta \theta$	= temperature rise in cell due to application of a calibration pulse of heat (K)
θ_{bath}	= bath temperature (K)
λ	= slope of the change in the heat transfer coefficient with time
ν_i	= stoichiometric coefficients
σ_n	= sample standard deviation of a given temperature measurement (K)
χ^2	= sum of inverse variance weighted deviations between experimental data and values predicted by the model using the nonlinear regression fitting algorithm
ψ	= slope of the change of cell potential with temperature (V)

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