

Calorimetric Principles and Problems in Pd-D₂O Electrolysis

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ABSTRACT

Most of the laboratories involved with the question of excess enthalpy in Pd-D₂O electrolysis experiments have employed isoperibolic calorimetric techniques. A careful re-examination of earlier results from several laboratories (California Institute of Technology, Massachusetts Institute of Technology, and Harwell Laboratory) is needed in terms of our present understanding of electrochemical calorimetry. Error sources in their experiments are discussed. There is possible evidence for excess power production in the Pd-D₂O electrolysis experiments at one of these laboratories.

A significant experimental problem in many isoperibolic calorimetric studies is the fact that the decrease in the electrolyte level due to electrolysis produces a significant decrease in the calorimetric cell constant if the temperature is measured in the electrolyte of the electrochemical cell. Furthermore, heat conduction pathways out of the top of the cell can produce large errors, especially at low power levels. There is no steady state in electrochemical calorimetry, hence accurate results require the evaluation of all terms in the differential equation governing the calorimeter.

1. Introduction

A critical assumption made by many laboratories is the steady state approximation for their isoperibolic calorimetric system. In point of fact there is no steady state during electrolysis experiments for either the cell voltage or the cell temperature. Exact calorimetric measurements, therefore, require the solution of the non-linear, inhomogeneous differential equation that governs the behavior of the calorimeter. Approximate solutions require, at the very least, an experimental evaluation of the terms involving the time-dependency of the cell temperature, cell voltage, and cell contents. This has not been done by most laboratories reporting electrochemical calorimetric results including studies by N. S. Lewis et. al., D. E. Williams et. al, D. Albagli et. al., and R. H. Wilson et. al.

Based on the isoperibolic calorimetric cells used at our laboratory, other major error sources arise from heat flow pathways through the top of the cell, room temperature changes, fluctuations in the cell voltage due to gas bubble effects, and changes in the liquid levels both within the cell and in the water bath. The convection-heat-transfer coefficient for air or other gases is 20-40 times smaller than for water according to L. C. Thomas.

Calorimetric accuracy is improved by systems of small volume with one short dimension and by intense stirring, thus long, thin, cylindrical calorimeters are favored by M. Fleischmann et. al. The significance of these calorimetric principles and problems were not obvious when several laboratories reported their failure to observe any excess power in 1989.

2. Methods

The sloping baseline is a significant problem in most isoperibolic calorimetric studies. The decrease in electrolyte level and the corresponding increase in gas volume in the headspace produces a calorimetric cell constant that decreases with time. We observed this major effect very early in our calorimetric studies (see D. E. Stilwell et. al.). An example of this large electrolyte-level effect is shown in Figure 1 for a Dewar-type calorimeter where the temperature is measured directly in the electrolyte. Other early investigators also noted this obvious effect including D. E. Williams et. al. and D. Albagli et. al., but it is a very surprising that no mention of this electrolyte-level effect was reported in the calorimetric studies by N. Lewis et. al. despite their extensive discussions of factors that may affect the calorimetric measurements. Calorimetric cell designs where the temperature is measured at a secondary liquid or solid phase at the outside surface of the electrochemical cell minimizes this sloping baseline problem as shown by D. E. Stilwell et. al. Our present calorimetric cell design and positions of the thermistors used for cell

temperature measurements remains virtually unchanged from our previous reports (see M. H. Miles et. al.). In our experiments, the electrolyte level has very little effect on our calorimetric cell constant.

3. Results

The time dependence of cell potentials and cell temperatures for two simultaneous experiments (cells A and B) are shown in Figure 2. Since the bath temperature is constant, changes in ΔT reflect changes in the cell temperature. Note that there is never any steady state for either the cell temperature or cell voltage, although the changes in both are approximately linear with time. The additions of D_2O produces sudden changes in the cell voltages following which there would be no valid calorimetric measurements for several hours (the time constants for these calorimetric cells are about 25 minutes).

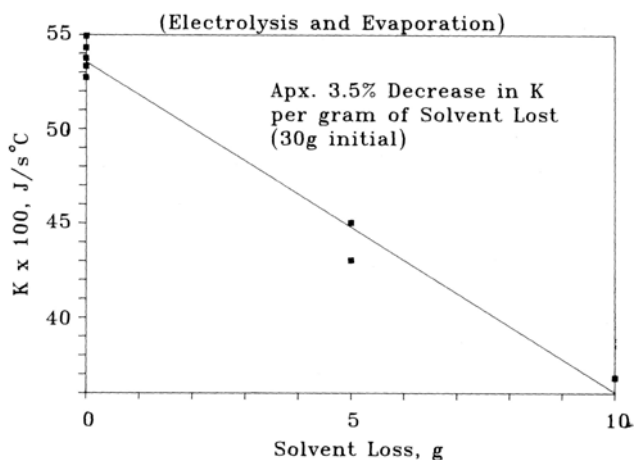


Figure 1. Decrease in the calorimetric cell constant due to solvent losses.

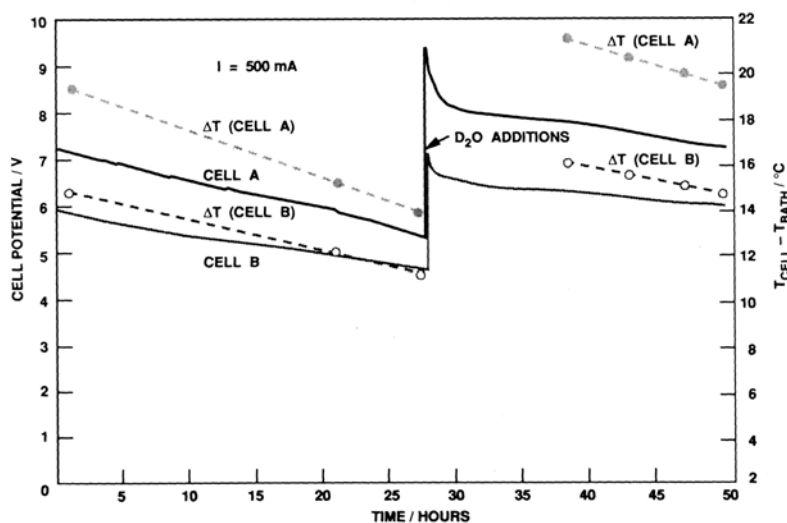


Figure 2. Time dependence of cell potentials and cell temperatures for cells A and B before and after D_2O additions.

The differential equation governing the behavior of our calorimeter can be expressed as

$$(E(t) - \gamma E_H) \bullet I + P_X = a + K \bullet \Delta T + P_{gas} + P_{calor} \quad (1)$$

where P_X represents any excess power. This equation also assumes that the bath and room temperatures are constant and that any power effects due to the deuterium loading or deloading of the palladium are negligible. The rate of enthalpy transfer outside the cell due to the D_2 , O_2 , and D_2O gas stream (P_{gas}) is given by

$$P_{gas} = \frac{\mathcal{M}}{F} \left\{ \left[0.5C_{P,D_2} + 0.25C_{P,O_2} + 0.75 \left(\frac{P}{P^* - P} \right) C_{P,D_2O(v)} \right] \Delta T + 0.75 \left(\frac{P}{P^* - P} \right) L \right\} \quad (2)$$

and the time-dependence of the enthalpy of the calorimeter is given by

$$P_{calor.} = C_{P,D_2O(l)} \left[M^\circ - (1 + \beta) \frac{\mathcal{M}t}{2F} \right] \frac{d\Delta T}{dt} - (1 + \beta) \frac{\mathcal{M}}{2F} C_{P,D_2O(l)} \Delta T \quad (3)$$

These expressions are essentially the same as given by Fleischmann et. al.

For our calorimeter at typical conditions of 0.2 M LiOD and $I = 500$ mA, we calculate $P_{gas} = 0.01$ W and $P_{cal} = -0.005$ W using experimental measurements of ΔT and $d\Delta T/dt$. Although P_{gas} and P_{cal} vary significantly with I and the electrolyte concentration, their sum remains positive and less than 0.020 W for our range of experimental conditions. Therefore, the neglect of the sum $P_{gas} + P_{calor.}$ in Equation 1 will only underestimate our value for P_X . Furthermore, other error sources in our calorimetry, such as room temperature fluctuations, contribute to an estimated error of ± 0.020 W. Calorimetric measurements of greater accuracy or over a wider range of experimental conditions, however, would require the solution of the differential equation (Eq. 1) as well as careful control of the bath and room temperatures.

It has been proposed by N. S. Lewis et. al. that a change in the rate and/or form of gas evolution can be a significant error source in electrochemical calorimetry. Therefore, our calorimetric cells were calibrated during electrolysis over a wide range of current densities (20-280 mA/cm²). Results of these calibrations are presented in Figures 3 and 4. At low currents ($I < 100$ mA), stirring by the electrolysis may not be sufficient while at high currents, any errors due to the neglect of the $P_{gas} + P_{calor.}$ terms in Eq. 1 become larger. Nevertheless, the correlation coefficients of 0.999 or better for each thermistor show excellent heat recovery for these calorimetric cells over the entire calibration range. The rate of gas evolution is not a significant calorimetric error source as suggested by N. Lewis.

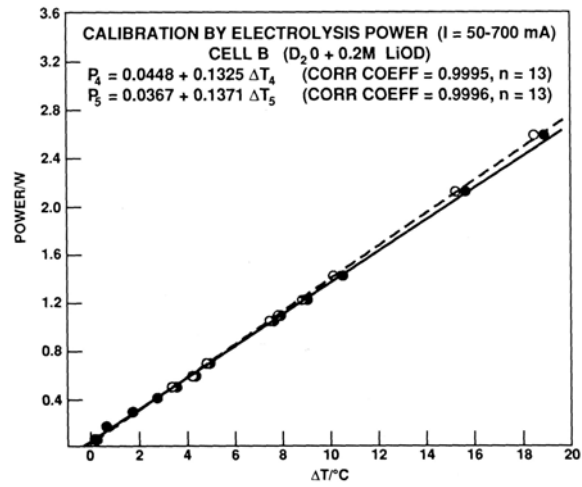


Figure 3. Calibrations for cell A by electrolysis power.

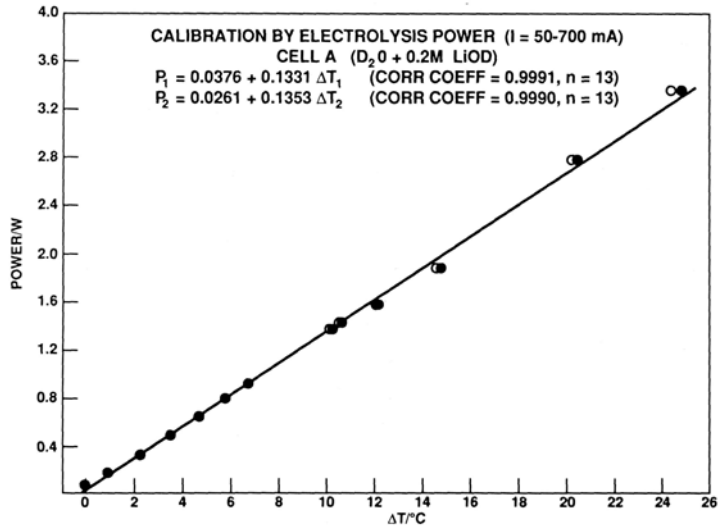


Figure 4. Calibrations for cell B by electrolysis power.

4. Discussion

For typical isoperibolic calorimetric cells, heat flows out of the top of the cell as well as into the constant temperature bath. Therefore, at constant bath and room temperature, it can be shown that

$$P = K_t(T_b - T_R) + K \cdot \Delta T \quad (4)$$

where $K = K_b + K_t$ (see M. H. Miles, R. A. Hollins et. al.). Thus there is a nonzero intercept for $\Delta T = 0$ as shown in Figures 3 and 4. The term $K_t(T_b - T_R)$ can become significant at low power levels, and the use of the approximate relationship $P \ll K \cdot \Delta T$ can produce large errors. This effect of the power level on the apparent cell constant (K) and heat transfer coefficient ($h = 1/k$) is shown in Figure 5 for our experimental results for thermistor 1 in cell A (Figure 3). The neglect of the intercept term in Equation 4 produces significant errors in the apparent cell constant for power levels below about 0.6 W. All of the calorimetric data reported by N. Lewis et. al. is near or below a total power level of 0.6 W, hence his use of the approximate relationship, $P \ll \Delta T/h$, is likely a large source of error. The schematic of the calorimetric cell design used at the California Institute of Technology as reported by G. M. Miskelly et. al. shows a relatively large area exposed to the ambient temperature, hence the problem of heat flow out of the cell top would be quite significant. Surprisingly, no mention of this large error source is discussed by N. S. Lewis.

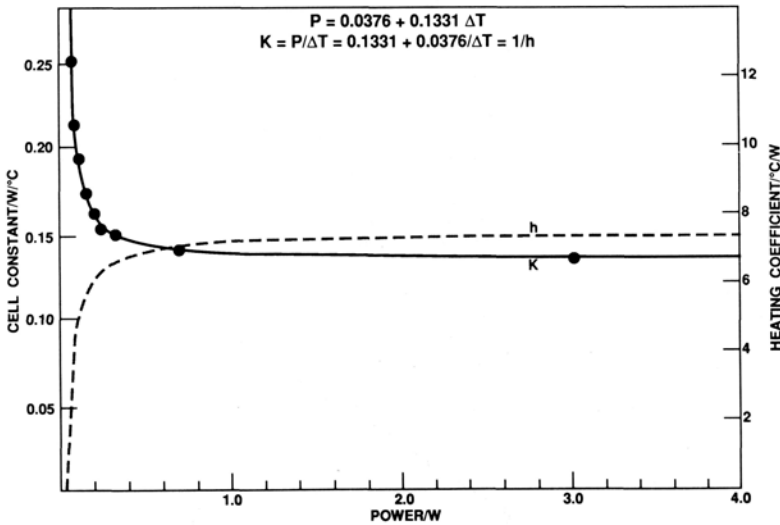


Figure 5. Effect of the power level on the apparent cell constant (K) and heat transfer coefficient (h).

A summary of our determinations of calorimetric cell constants over a three-year period is presented in Table 1. Except for the first three studies, these cell constants are based on Equation 4 rather than the approximate relationship, $P \approx K \cdot \Delta T$. There is no significant change of these cell constants over this time period. Calibrations were performed in D_2O as well as H_2O and by Joule heating (20-ohm resistor) as well as by electrolysis, yet excellent agreement is observed. The small differences in the measured cell constants could be attributed to the different methods of calibration and to differences in the insulation of the cell top from one experiment to another.

Table 1. Cell Constant Determinations.

Experiment	K ₁ (W/°C)	K ₂ (W/°C)	K ₄ (W/°C)	K ₅ (W/°C)	Date
Pd/D ₂ O	0.141	0.145	0.133	0.132	1989
Pd/H ₂ O	0.135	0.138	0.137	0.134	1989
Pd/D ₂ O	0.139	0.143	0.133	0.134	1990
Joule heating* (D ₂ O)	0.136	0.144	0.136	0.138	1990
Joule heating* (D ₂ O and H ₂ O)	0.141	0.148	0.132	0.133	1991
Pd/D ₂ O*	0.136	0.137	0.136	0.140	1991
Pd/D ₂ O*	0.143	0.143	0.141	0.141	1992
Mean	0.139	0.143	0.135	0.136	
	±0.003	±0.004	±0.003	±0.004	

* Calculated for P = 2.00 W.

In striking contrast to the stability of calorimetric cell constants in our experiments, N. Lewis et. al. report heat transfer coefficients that range from 12.6°C/W in H₂O to 15.9°C/W after 115 hours of D₂O electrolysis. This 26% increase in heating coefficients, based on our experience, is highly unusual. Closer examination, however, shows that N. Lewis et. al. erroneously define the heating coefficient as $h = \Delta T/P_T$ where the total power (P_T) is the sum of the electrolysis power + resistor power. According to the Newton law of cooling, the temperature difference, ΔT , defines the total output power from the cell to its surroundings, thus any excess power (P_X) must be included in defining the total power. This neglect of P_X by N. Lewis et. al. in the equation defining h would lead to an increase in the heating coefficient as the excess power increases. An analysis of this error in the N. Lewis study is presented in detail by M. H. Miles, R. A. Hollins et. al.

Table 2 presents an analysis of the results reported by N. Lewis et. al. when a constant heating coefficient of 14.0°C/W is assumed. Initially, there is no excess power. However, as electrolysis continues an excess power effect develops that becomes as large as 0.076 W after 161 hours of Pd/D₂O + LiOD electrolysis. The excess power density of 1.0 W/cm³ Pd for this analysis of the N. Lewis study is in excellent agreement with our experiments (1.3 W/cm³ Pd at 200 mA/cm²) as well as with the results reported by M. Fleischmann et. al. in 1990.

In the calorimetric studies by N. Lewis et. al., a series of duplicate experiments (A, B, C, D, E) were conducted where a portion of the electrolysis power (P_{EL}) was replaced by resistor power (P_{Re}) in a manner that maintained the cell temperature essentially constant as shown in Table 2. Thus

$$P_T = P_{EL} + P_X \quad (5)$$

in one experiment where no resistor power is used ($P_{Re} = 0$), and

$$P'_T = P'_{EL} + P'_X + P'_{Re} \quad (6)$$

in the second experiment with $P'_{EL} < P_{EL}$ and $P'_T \approx P_T$. Thus

$$\Delta P_T = P_T - P'_T = P_{EL} - P'_{EL} + P_X - P'_X - P'_{Re} \quad (7)$$

For a constant cell temperature, the total output power must remain constant ($\Delta P_T = 0$), thus from simple algebra

$$P_X - P'_X = P'_{EL} + P'_{Re} - P_{EL} \quad (8)$$

The experimental observation by N. Lewis that $P'_{EL} + P'_{Re} \approx P_{EL}$ simply cannot prove that there is no excess power but only that $P_X - P'_X \cong 0$, i.e., the change in P_X is small when a portion of the electrolysis power is replaced by resistor power. It is interesting to note from Table 2 that the input power ($P_{EL} + P_{Re}$) required to maintain a constant cell temperature in the Lewis study is always smaller for the experiment at the higher current density. This effect is consistent with the presence of an anomalous excess power that increases with the current density and is near the magnitude reported by Fleischmann et. al. A similar error analysis of the N. Lewis calorimetry has been previously provided by V. C. Noninski and C. I. Noninski.

Table 2. Analysis of Cal Tech Calorimetric Results.^a

$$P_{out} = (T_{cell} - 25.30)/h \text{ where } h = 14.0^\circ\text{C/w}$$

Exp. Time (h)	Current Density		T_{cell} ($^\circ\text{C}$)	P_{in} (W)	P_{in} (W)	P_X (W)	
	(mA/cm ²)						
A-1	14.7		108	31.80	0.464	0.463	0.001 ^b
A-2	16.0		74	31.82	0.466	0.467	-0.001
B-1	63.7		74	32.04	0.481	0.442	0.039
B-2	66.0		110	32.01	0.479	0.429	0.050 ^b
C-1	88.7		110	34.69	0.671	0.619	0.052
C-2	94.5		140	34.64	0.667	0.607	0.060 ^b
D-1	113.2		72	32.13	0.488	0.433	0.055
D-2	115.0		108	32.08	0.484	0.426	0.058 ^b
E-1	161.0		140	34.69	0.671	0.595	0.076 ^{b,c}
E-2	164.5		115	34.71	0.672	0.600	0.072

^a N. S. Lewis, et. al., *Nature*, 340. 525 (1989).

^b Higher current density.

^c $P_X/V_{Pd} = 0.076 \text{ W}/0.073 \text{ cm}^3 = 1.04 \text{ W/cm}^3$ (0.054 W/cm²)

In contrast to the Lewis experiments, the calorimetric studies by D. E. Williams et. al. and D. Albagli et. al. identified the importance of the electrolyte level effect and the problem of the heat flow pathway through the top of the cell to the ambient atmosphere. However, both these studies invoke steady state approximations as well as questionable cell calibration procedures. The calorimetric error ranges of ± 40 mW for the M.I.T. studies and $\pm 15\%$ excess power ($\pm 2\sigma$) for the Harwell calorimetry fall far short of the ± 1 mW accuracy reported by M. Fleischmann et. al. Both the Harwell and M.I.T. laboratories report calorimetric measurements over rather short time periods (100 hours for M.I.T. and one experiment lasting only 8 hours for Harwell). We have never observed any excess power in less than 6 days in our experiments involving Pd/D₂O + LiOD electrolysis.

A summary of additional error sources and problems for the study by D. E. Williams et. al. include their method of cell calibration during electrolysis when any excess power is unknown, their large power changes used during calibrations, the marked endothermic behavior following topping up of their cells with D₂O, and their use of small electrodes in large electrolyte volumes that would minimize the detectability of any excess power effect as well as contribute to poor stirring and possible H₂O contamination in these large cells. Furthermore, the unfavorable geometry of various cathodes (beads, ribbon, bar) would not provide for uniform electric fields and symmetry required for high deuterium loadings. These numerous error sources call into question any calorimetric conclusions stemming from the Harwell experiments.

5. Conclusions

The early cold fusion calorimetric results by several major laboratories in 1989-1990 contain serious errors that will ultimately undermine the acceptance of these studies as credible electrochemical calorimetry. These publications by N. Lewis, D. E. Williams, D. Albagli and others, however, serve to illustrate important

calorimetric principles, problems, and sources of error relating to attempts to measure excess power in the Pd-D₂O system. Electrochemical calorimetric measurements accurate to within ± 1 mW require the integration of the differential equation governing the calorimeter as well as careful control of external experimental conditions such as the ambient laboratory temperature.

6. Acknowledgments

We thank Drs. Vesco C. Noninski and Joseph L. Waisman for helpful discussions relating to the calorimetric results reported by various laboratories.

7. List of Symbols/Nomenclature

a	=	$K_t (T_b - T_R)$, power intercept for $\Delta T = 0$, W
C_p	=	Heat capacity at constant pressure, $\text{JK}^{-1}\text{mol}^{-1}$
E_H	=	Thermoneutral potential, V
$E(t)$	=	Measured cell potential at time, t, V
F	=	Faraday constant, 96485 C mol^{-1}
h	=	Apparent heat transfer coefficient due to conduction, K/W
I	=	Cell current, A
K	=	Apparent calorimetric cell constant due to conduction, W/K
K_b	=	Calorimetric cell constant for heat flow from the cell into the bath, W/K
K_t	=	Calorimetric cell constant for heat flow out of the top of the cell, W/K.
L	=	Enthalpy of evaporation, J mol^{-1}
M°	=	Heavy water equivalent of the calorimetric when topped up, mol
P	=	Partial pressure, Pa
P^*	=	Atmosphere pressure, Pa
P_{calor}	=	Rate of enthalpy change within the calorimeter, W
P_{EL}	=	Power input due to electrolysis, W
P_{gas}	=	Rate of enthalpy transport by the gas stream, W
P_{Re}	=	Power input due to calibration heater, W
P_X	=	Excess power, W
T_b	=	Temperature of bath, K
T_{cell}	=	Temperature measured at the outer wall of the electrolysis cell, K
T_R	=	Temperature of room (ambient), K
ΔT	=	$T_{\text{cell}} - T_b$, K
β	=	Dimensionless term allowing for D ₂ O losses by evaporation or other means besides electrolysis
γ	=	Current efficiency for D ₂ O electrolysis
σ	=	Standard deviation for series of measurements

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