PRECISION AND ACCURACY OF COLD FUSION CALORIMETRY

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Introduction

The cold fusion controversy centers on the precision and accuracy of the calorimetric systems used to measure excess enthalpy generation.[1-3] For open, isoperibolic calorimetric systems, there is no true steady state during D_2O+LiOD electrolysis. Exact calorimetric measurements, therefore, require modeling by a differential equation that accounts for all heat flow pathways into and out of the calorimetric systems.[1-8] The improper use and misunderstanding of this differential equation is a major source of confusion concerning cold fusion calorimetric measurements.[1,9-13]

The precision and accuracy of isoperibolic cold fusion calorimetry can be assessed by means of experiments on "blank systems" where no excess enthalpy generation due to cold fusion is expected. Therefore, a clean platinum (not palladium) cathode was polarized in D_2O+0.1M LiOD using platinum also as the anode. The only excess enthalpy generation expected would be from the recombination of the evolved D_2 and O_2 gases. Although the amount of recombination in cold fusion experiments has been a source of controversy,[2,3] various experimental studies have shown that the recombination effect is small at the large current densities used in cold fusion experiment.[2,3,9,14]

Materials and Methods

Calorimetric Cell

Long and narrow calorimetric cell designs promote rapid radial mixing of the electrolyte by the electrolysis gas evolution and minimize heat transfer through the top of the cell relative to the desired pathway through the cell wall to the water bath.[1,9] The use of Dewar cells makes the heat transfer pathway predominantly due to radiation across the vacuum gap of the Dewar cell. Therefore, the heat transfer coefficient can be calculated theoretically by the product of the Stefan-Boltzmann coefficient and the radiant surface area of the cell (109.7 cm^2 in these experiments). Multiplying by the Stefan-Boltzman coefficient, 5.6703×10^{-12} $Wcm^{-2}K^{-4}$, yields a theoretical heat transfer coefficient of 0.622×10^{-9} WK^{-4} for this cell. The Dewar cell used was approximately 2.5 cm in diameter (I.D.) and 22.0 cm in height with the upper 8.0 cm silvered to minimize the effect of the electrolyte level.[1,9]

The platinum cathode used in these experiments was 0.1 cm in diameter and 2.0 cm in length (A=0.63 cm^2). The temperature of the thermostated water bath (approximately 21°C) was precisely controlled to ±0.01°C.

Calorimetric Equations

From basic thermodynamic principles, the calorimetric cell is the system of interest, and the First Law of Thermodynamics expressed as power (J/s or W) becomes

$$P_{calor} = P_{EI} + P_H + P_X + P_{gas} + P_R + P_C + P_W \qquad (1)$$

Equation 1 represents the differential equation used to model this open, isoperibolic calorimetric system.

By definition, P_{EI} is the electrochemical power, P_H is the internal heater power, P_X is any anomalous excess power, P_{gas} is the power resulting from the gas stream (D_2, O_2, D_2O vapor), P_R is the power transferred by radiation from the cell to the water bath, P_C is the power transferred by conduction and P_W represents the rate of any pressure-volume work. As usual, positive quantities represent power added to the system (calorimetric cell) and negative quantities represent power given off to the surroundings. The mathematical expressions for these terms are as follows:

$$P_{calor} = C_p M(dT_{cell}/dt) \tag{2}$$

$$P_{EI}=(E(t)-E_H)I \tag{3}$$

$$P_{gas} = -(I/F)\{[0.5\ C_{P,D2}+0.25\ C_{P,\ O2}+0.75\ (P/(P^*\!-P))C_{P,D2O\ (v)}]\Delta T \\ + 0.75\ (P/(P^*\!-P))\ L\} \tag{4}$$

$$P_R=-k_R f(T)\ where\ f(T)=T_{cell}^{\ 4} - T_b^{\ 4} \tag{5}$$

$$P_C = -k_C\ (T_{cell} - T_b) \tag{6}$$

$$P_W = -RT\ (dn_g/dt) = -RT(0.75I/F) \tag{7}$$

Definitions for many of the symbols used are given elsewhere.[1,9]

Assuming P_C and P_W are relatively small compared to P_R, then

$$P_R^{'} =P_R+P_C+P_W=-k_R^{'} f(T) \tag{8}$$

where $k_R^{'}$ is the pseudoradiative heat transfer coefficient. The validity of this assumption can be determined by comparing $k_R^{'}$ with the theoretical value calculated from the Stefan-Boltzmann coefficient. By assuming $P_X=0$, a lower bound heat transfer coefficient can be evaluated using Eqs. 1 and 8.

$$(k_R^{'})_1 = (P_{EI}+P_H+P_{gas} - P_{calor})/f(T) \tag{9}$$

The presence of any excess power would increase $f(T)$, thus yielding a lower value for $(k_R^{'})_1$. For this blank experiment, P_X will be small, thus $(k_R^{'})_1$ will be close to the true value. By use of the 12 hour heating pulse, and assuming the excess power (P_X) is constant with time, the true heat transfer coefficient can also be evaluated

$$(k_R^{'})_2 = (P_{EI}+P_H+P_X+P_{gas}-P_{calor})/f(T) \tag{10}$$

Complete mathematical details are presented elsewhere.[9,11-13]

Analogous with differential equations for reaction kinetics, more accurate calorimetric results can be obtained by the integration of the data sets.[11-13] Both forward and backward integration methods were used with the calorimetric differential equations (Eq. 1). A variety of methods, therefore, can be used to evaluate the

pseudoradiative heat transfer coefficient including lower bound, true, differential, forward integration and backward integration techniques.[9-13]

Each experimental cycle lasted exactly two days over a total of 16 days. For each cycle, the internal cell heater was off for 12 hours, then turned on at $t=t_1$, for 12 hours and then off at $t=t_2$ for the final 24 hours. Addition of D_2O occurred at the beginning of each cycle. The cell current was constant at 0.2000 A.

Results and Discussion

Various methods were used to evaluate the pseudoradiative heat transfer coefficient, $k_R^{'}$, at $t=t_2$ for each two-day experimental cycle. For example, mean values were $(k_R^{'})_1 = 0.62013 \times 10^{-9}$ WK^{-4} (lower bound, Eq. 9) and $(k_R^{'})_2 = 0.62059 \times 10^{-9}$ WK^{-4} (true, Eq. 10). The most accurate method for determining $k_R^{'}$ was backward integration that yields a mean value of $(k_R^{'})_{262}^0 = 0.62083 \times 10^{-9}$ WK^{-4} for this calorimetric cell. All values obtained for $k_R^{'}$ were close to the theoretical result of 0.622×10^{-9} WK^{-4} calculated from the Stefan-Boltzmann coefficient, and this result validates the assumption made in Eq. 8.

The two calorimetric experimental parameters required for Eq. 1 are $k_R^{'}$ and the water equivalent of the system, C_pM. For integration, the calorimetric equation (Eq. 1) can be written in a straight line form, y=mx+b, where the intercept yields $k_R^{'}$ and the slope is C_pM [9-13]. The various integration methods yield an over-all mean value of $C_pM = 340.1 \pm 0.8$ JK^{-1}. This is the least accurate calorimetric parameter, but its effect can be minimized by evaluations made at the end of the heating pulse ($t=t_2$) where $CpM\ (dT_{cell}/dt) \approx 0$. Theoretical calculations based on the mass of heavy water used and the glass and metal components in contact with the electrolyte give C_pM values in approximate agreement with the experimental values.[9]

The differential rate of excess enthalpy production due to recombination in this blank system can be estimated from the equation obtained by subtracting Eq. 9 from Eq. 10

$$P_X = \left[(k_R^{'})_2 - (k_R^{'})_1 \right] f(T) \tag{11}$$

This estimate yields $P_X = 0.6$ mW. The more accurate calorimetric results using integration methods yields $P_X = 1.1 \pm 0.1$ mW for recombination in these experiments. Theoretical calculations using Henry's Law and Fick's Law of Diffusion yield approximately 1 mW due to the reduction of oxygen at the cathode in this electrolysis system. The electrochemical oxidation of deuterium or hydrogen does not occur at the platinum oxide surface of the anode.

The ability of this calorimetry to measure excess power within ± 0.1 mW with an enthalpy input to the cell of approximately 800 mW demonstrates a precision of 99.99%. Additional evaluations show that the accuracy of this calorimetry is also close to 99.99%. The logical conclusion from the control study is that excess enthalpy measurements using this cold fusion calorimetric system cannot be scientifically dismissed as calorimetric errors.

Palladium-boron alloy materials prepared at the Naval Research Laboratory (NRL) have shown a remarkable ability to produce the excess power effect.[9,15] A calorimetric system similar to the system used in this blank study yielded excess power effects in the range of 100 to 400 mW over a 50 day period in experiments using a

Pd-B cathode.[9] The measured excess power increased to over 9 W (9000 mW) during the final boil-off phase.[9] Excess power continued for several hours after this Pd-B cell boiled dry.[9]

References

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5. Fleischmann, M, Pons, S., Anderson, M.W., Li, L.J., Hawkins, M. (1990). *J. Electroanal. Chem*., **287**, 293.
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9. Miles, M.H., Fleischmann, M. and Imam, M.A. (2001). Naval Research Laboratory Report Number NRL/MR/6320-01-8526, March 26, 2001.
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11. Fleischmann, M. and Miles, M.H. (2006). In "Condensed Matter Nuclear Science", pp. 247-268, P.L. Hagelstein and S.R. Chubb, Editors, World Scientific, New Jersey, ISBN No. 981-256-564-7.
12. Fleischmann, M. and Miles M.H. (2006). Manuscript No. JP058292J submitted to *J. Phys. Chem.* Note: Editor George C. Schatz rejected this manuscript and ruled that the two reviewers did not need to respond to the detailed rebuttal by the authors to the reviewers comments.
13. Szpak, S. and Mosier-Boss, P.A. (2006). SPAWAR System Center Technical Report, San Diego, CA (in press). Note: Contains complete *J. Phys. Chem.* manuscript (Ref. 12) as well as comments of the two reviewers and the unanswered rebuttal of these comments by the authors.
14. Will, F.G. (1997). *J. Electroanal. Chem*., **426**, 177.
15. Miles, M.H. and Imam, M. Ashraf (2004). U.S. Patent Number 6,764,561   June 20, 2004.

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OBJECTIVES

Establish Thermal Balance For A Blank System (Pt/D$_2$O)

(0.01% Error)

- **Precision of ±0.1 mW for 800 mW Input**

- **Measure Excess Power From Oxygen Reduction**

  (Recombination)
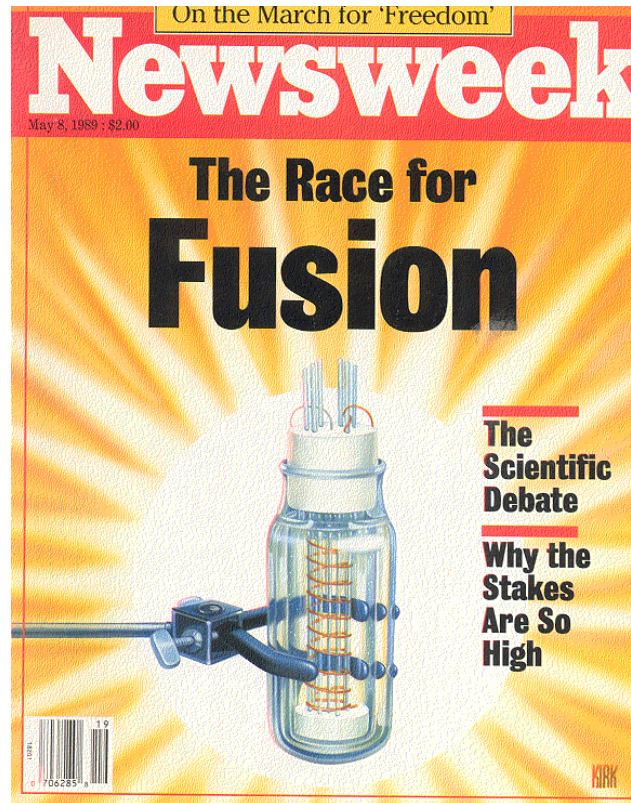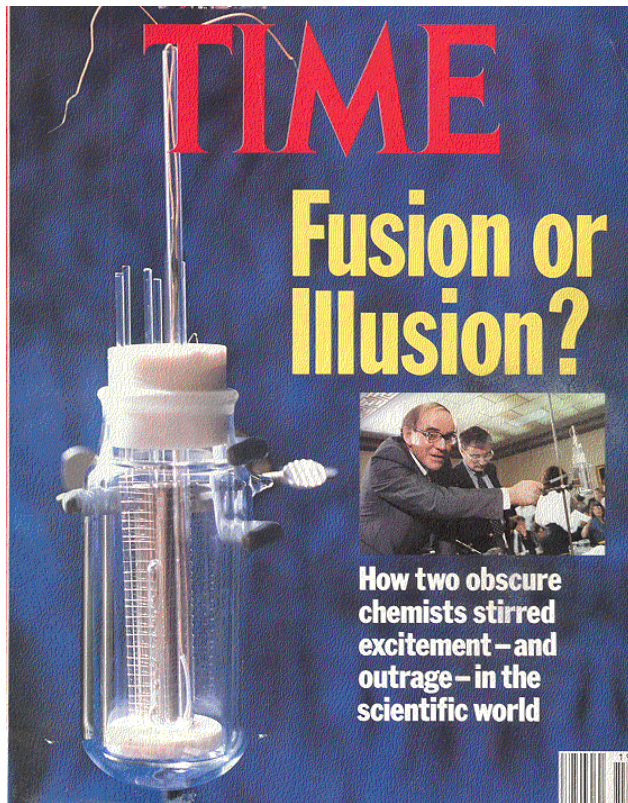
(1.1 mW)

Compare With Pd-B/D$_2$O System

- **Excess Power of 50 to 500 mW**

- **Increase of Excess Power to 10 W During Boil-Off**

Explain The Different Behavior of Pt/D$_2$O and Pd-B/D$_2$O
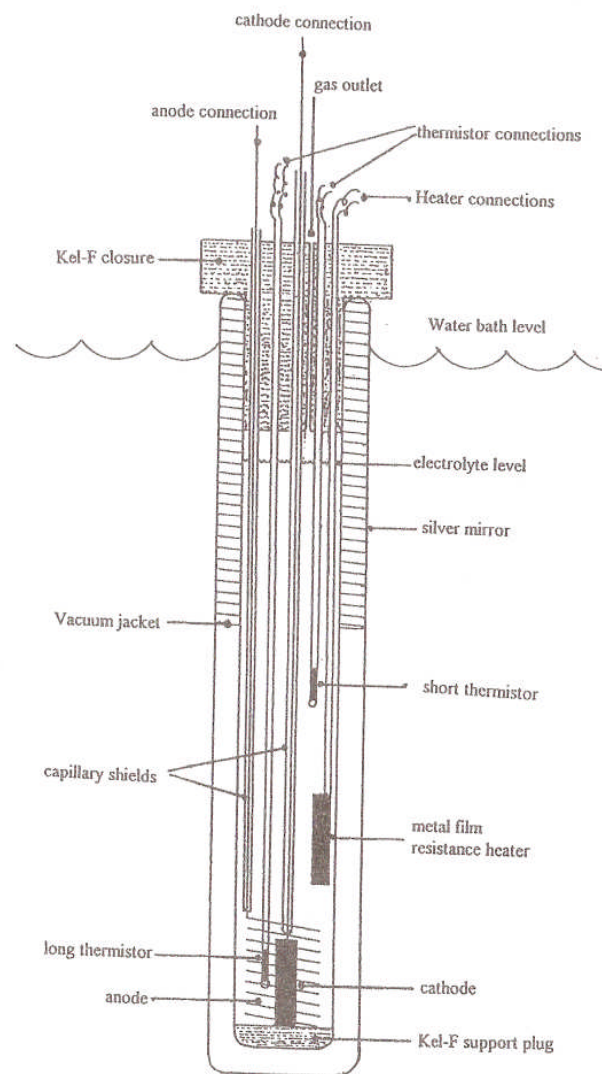
$$^2_1 D + {}^2_1 D \rightarrow {}^4_2 He + 23.8 \text{ MeV}$$

Magazine Cover Stories
8 May 1989
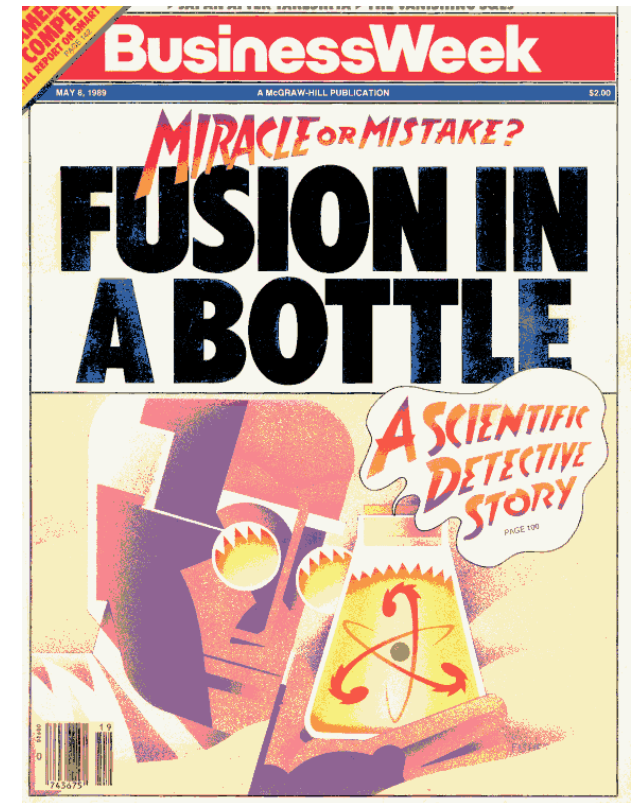
TRULY EXTRAORDINARY INTEREST

ISOPERIBOLIC DEWAR CALORIMETRY CELL

cathode connection

gas outlet

anode connection

thermistor connections

Heater connections

Kel-F closure

Water bath level

electrolyte level

silver mirror

Vacuum jacket

short thermistor

capillary shields

metal film resistance heater

long thermistor

cathode

anode

Kel-F support plug

FUSION ENERGY CALCULATION

$$^{2}_{1}D + ^{2}_{1}D \longrightarrow ^{4}_{2}He + 23.8 \text{ MeV}$$

$(1.5 \times 10^{43} \text{ D atoms})(\frac{1 fusion}{2 D atom})(23.8 \times 10^{6} \frac{eV}{fusion})(1.602 \times 10^{-19} \frac{J}{eV}) = 2.9 \times 10^{31}$ J

Energy per person per year (USA)

$(10.0 \frac{kW}{person})(1000 \frac{W}{kW})(365 \frac{days}{year})(24$ hr/day$)(60$ min/hr$)(60$ s/min$) = 3.15 \times 10^{11}$ J

World (7 billion) Energy per year

$(7 \times 10^{9})(3.15 \times 10^{11}$ J$) = 2.2 \times 10^{21}$ J/year

Years Fueled by D + D Fusion

$(2.9 \times 10^{31}$ J$) / (2.2 \times 10^{21}$ J/year$) = 1.3 \times 10^{10}$ years

(13 billion years!)

HEAT TRANSFER PATHWAYS
POWER (J/S OR W)

Calorimetric System, P_{calor}

Electrochemical Power, P_{El}

In-Cell Heater Power, P_H

Anomalous Excess Power, P_X

Gas Evolution Power, P_{gas}

Heat Radiation Power, P_R

Heat Conduction Power, P_C

Rate of Work Done By Gases, P_W

CALORIMETRIC EQUATIONS
(First Law of Thermodynamics)

$$0.5 \ D_2O_{(l)} \rightarrow 0.5 \ D_{2(g)} + 0.25 \ O_{2(g)}$$

$$P_{calor} = P_{EI} + P_H + P_X + P_{gas} + P_R + P_C + P_W$$

where

$$P_{calor} = C_P M \ (d \ T_{cell}/dt)$$

$$P_{EI} = (E(t) - E_H) \ I$$

$$P_{gas} = -(I/F)\{[0.5 C_{P,D2}+0.25 C_{P,02}+0.75(P/(P^*-P))C_{P,D2O(v)}]\Delta T+0.75(P/(P^*-P))L\}$$

$$P_R = -k_R f(T) \ \text{where} \ f(T)=T^4_{cell}-T_b^4$$

$$P_C = -k_C(T_{cell}-T_b)$$

$$P_W = -RT(dn_g/dt)=-RT(0.75I/F)$$

FLEISCHMANN'S DEWAR CALORIMETRY

$$P_R \gg (P_C + P_W)$$

$$P'_R = P_R + P_C + P_W = -k'_R f(T)$$

Thus

$$P_{calor} = P_{El} + P_H + P_X + P_{gas} + P'_R = P_{El} + P_H + P_X + P_{gas} - k'_R f(T)$$

<u>**Lower Bound Heat Transfer Coefficient (Assume $P_X=0$)**</u>

$$(k'_R)_1 = (P_{El} + P_H + P_{gas} - P_{calor})/f(T)$$

<u>**True Heat Transfer Coefficient (Assume P_X is Constant)**</u>

$$(k'_R)_2 = (P_{El} + P_H + P_X + P_{gas} - P_{calor})/f(T)$$

$$P_X = [(k'_R)_2 - (k'_R)_1]f(T)$$

THEORETICAL RADIATIVE HEAT TRANSFER COEFFICIENT

Stefan-Boltzmann Coefficient

$$k_B = 5.6703 \times 10^{-12} \; Wcm^{-2}K^{-4}$$
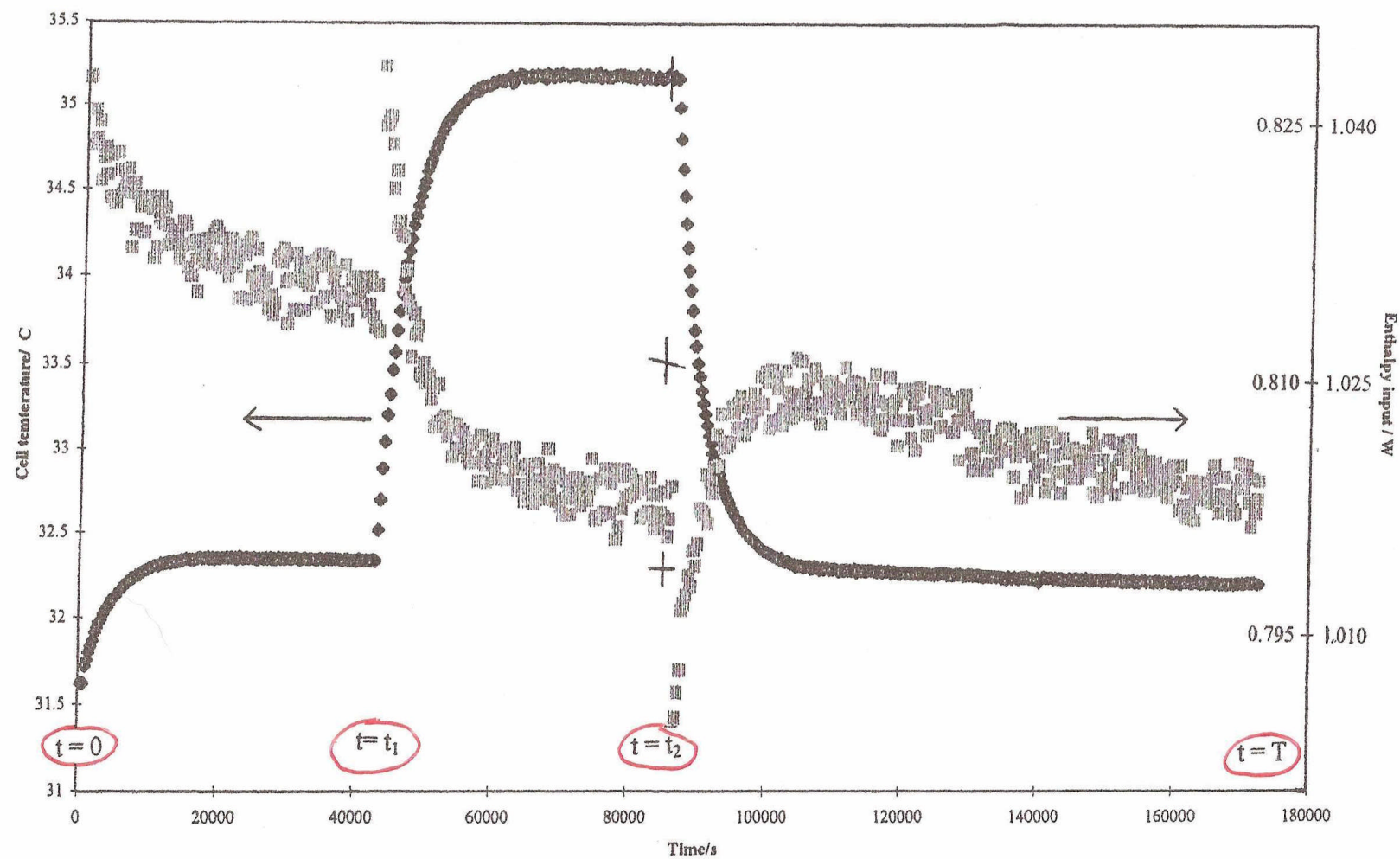
Radiant Surface Area of Cell

$$A = 109.7 \; cm^2$$

Theoretical Radiative Heat Transfer Coefficient

$$k_R = k_B \, A = (5.6703 \times 10^{-12} \; Wcm^{-2}K^{-4})(109.7cm^2)$$

$$k_R = 0.622 \times 10^{-9} \; WK^{-4}$$

RAW DATA FOR DAYS 9 AND 10
(I = 0.200 A)

EVALUATION OF $(k'_R)^2$ AT $t=t_2$

$$(k'_R)_2 \; f(T)(t_2) = (P_{El} + P_H + P_X + P_{gas} - P_{calo}r)(t_2) \qquad (1)$$

$$(k'_R)_2 \; f(T)(t'_2) = (P_{El} + P_X + P_{gas} - P_{calor})(t'_2) \qquad (2)$$

Assume P_X is constant

(1) – (2) yields

$$(k'_R)_2 \; f_2(T) = [P_{El}(t_2) - P_{El}(t'_2)] + P_H$$
$$+ [P_{gas}(t_2) - P_{gas}(t'_2)]$$
$$- [P_{calor}(t_2) - P_{calor}(t'_2)]$$

where

$$f_2(T) = (T^4_{cell})t_2 - (T^4_{cell})t'_2$$

STRAIGHT LINE FORM
(Y = a+bX)

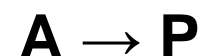$$(P_{EI}+P_H+P_X+P_{gas})/f(T) = (k'_R)_2+C_PM(dT_{cell}/dt)/f(T)$$

$$\text{Intercept} = (k'_R)_2$$

$$\text{Slope} = C_pM$$

$$f(T) = T^4_{cell} - T^4_b$$

CHEMICAL KINETICS ANALOGY

First Order Rate Law $\qquad\qquad$ $A \rightarrow P$

Differential Equation

$$-dA/dt = kA$$

Integrated Rate Law
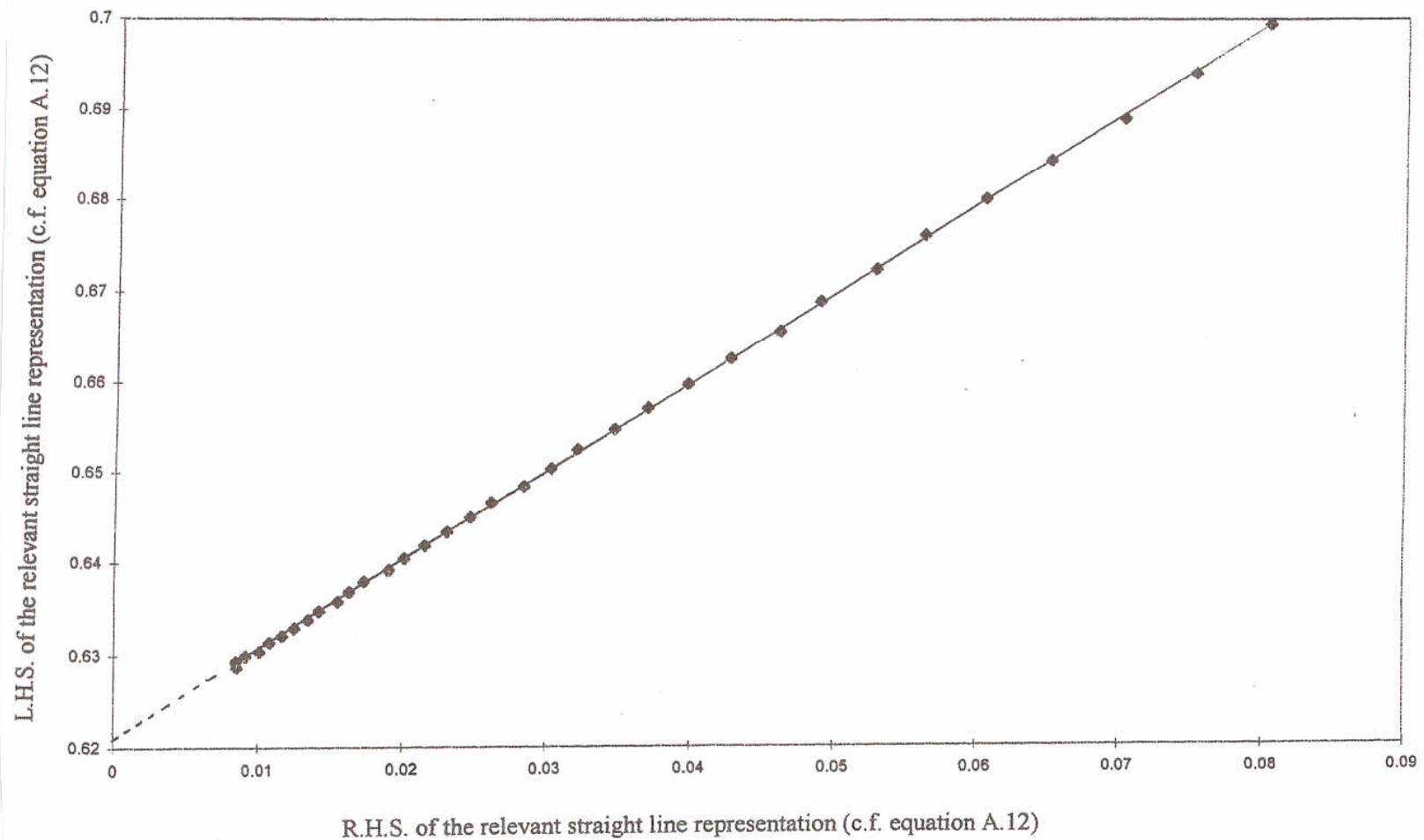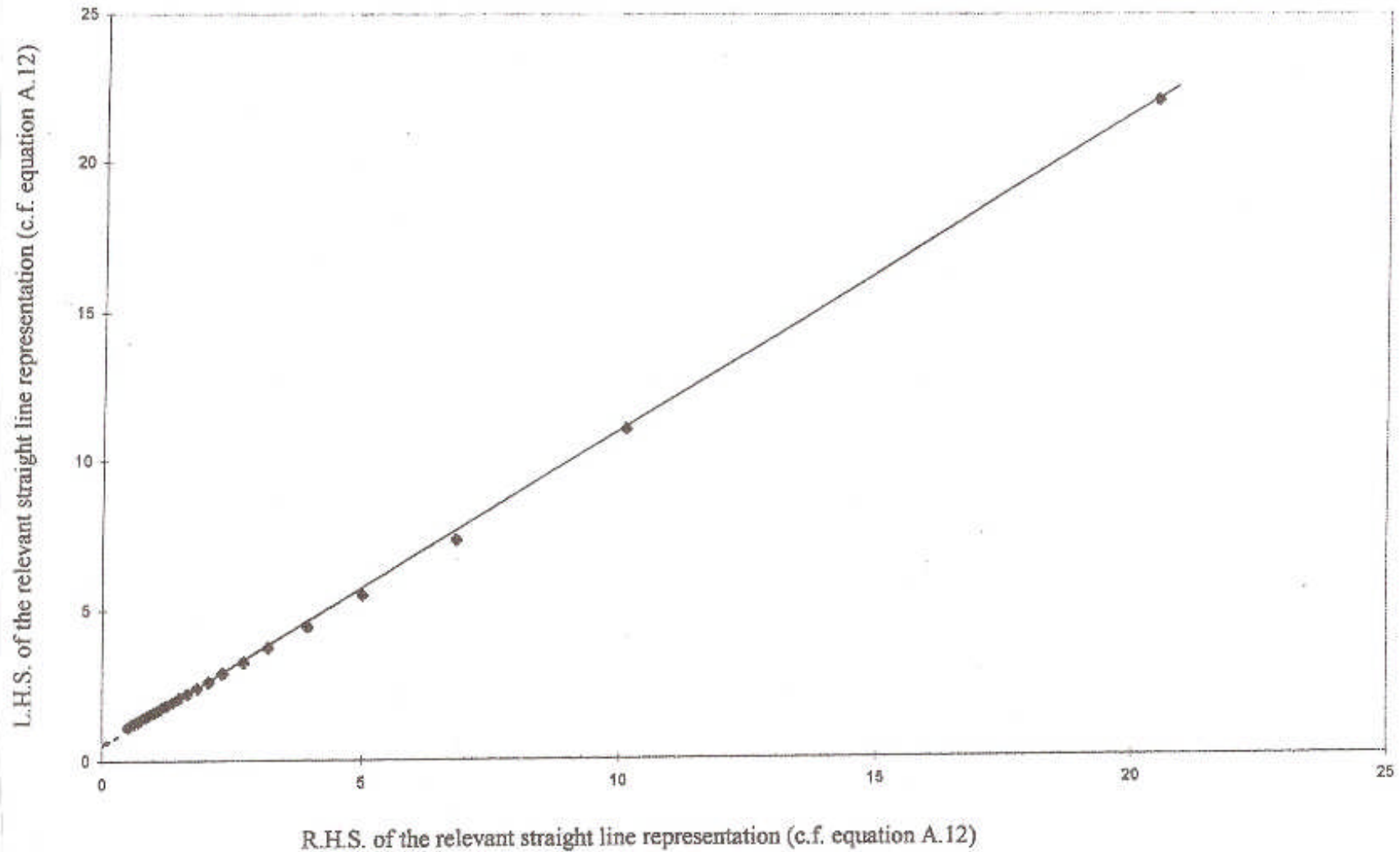
$$\ln A = \ln A_o - kt \qquad\qquad (y = a + bx)$$

$$slope = -k$$

$$Intercept = \ln A_o$$

# EVALUATION OF $(k_R')_{262}$ AND C_pM
(Backward Integration)

EVALUATION OF $(k_R')_{362}$ AND C_pM
(Forward Integration)

L.H.S. of the relevant straight line representation (c.f. equation A.12)

R.H.S. of the relevant straight line representation (c.f. equation A.12)

MEAN VALUES FOR K AND C_PM

Description	$10^9 (k'_R)$, WK^{-4}	C_PM, JK^{-1}
Theoretical	0.622	340
$(k'_R)_1$	0.62013	-----
(lower bound)	±0.00058	
$(k'_R)_2$	0.62059	-----
(true)	±0.00240	
$(k'_R)^0_{262}$	0.62083	339.2
(backward Integration,True)	±0.00059	±1.7
$(k'_R)^0_{362}$	0.62031	339.8
(forward Integration, True)	±0.00156	±18.3

EXCESS POWER DUE TO OXYGEN REDUCTION
(Differential / Integral)
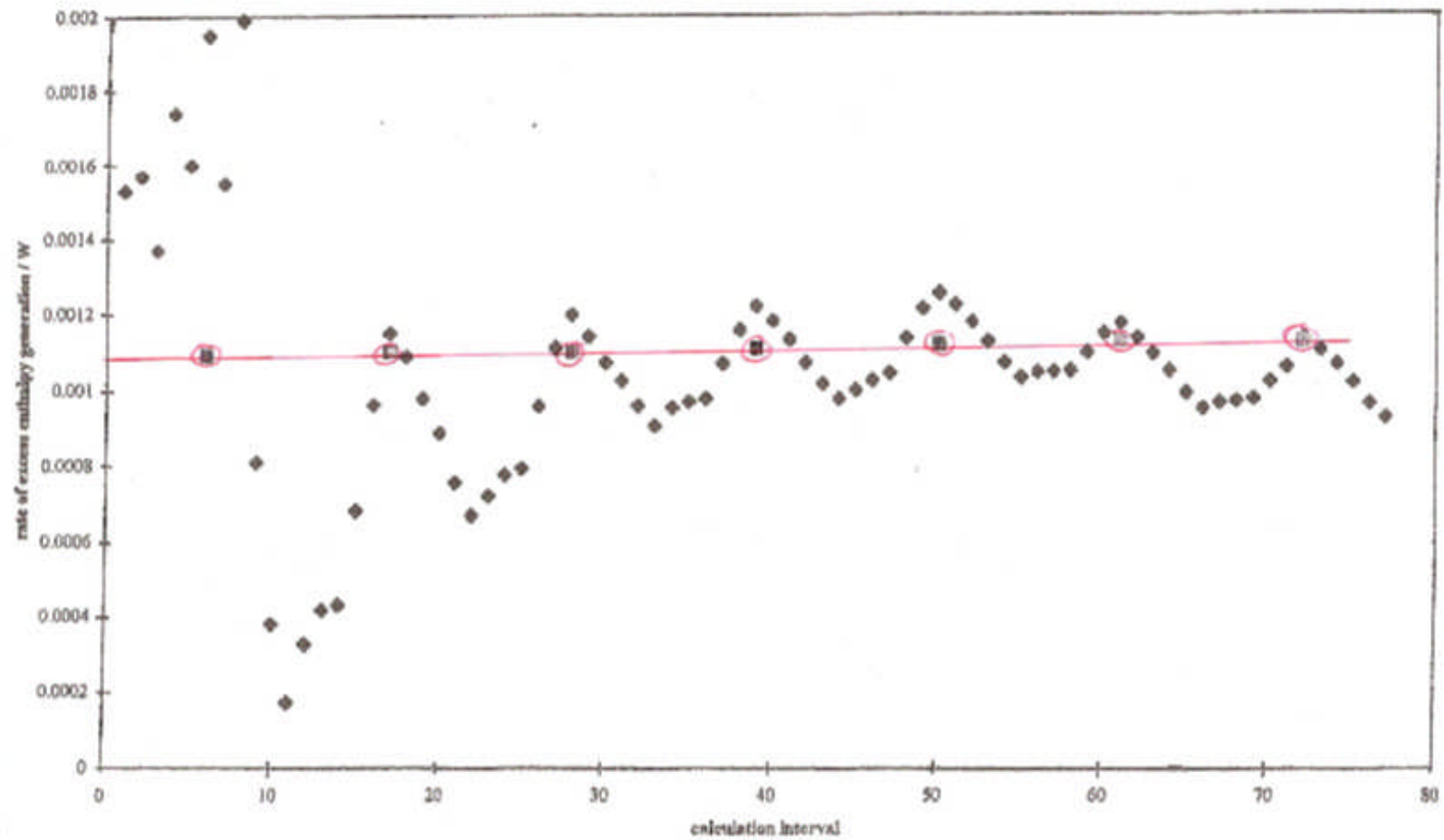
THEORETICAL RATE OF OXYGEN REDUCTION
EXCESS POWER

<u>Henry's Law</u> $[O_2] = 1.2 \times 10^{-3}$ $M = 1.2 \times 10^{-6}$ mol/cm³

<u>Fick's Law of Diffusion</u>

$I_L = DnF[O_2] A_E/\delta = 0.001A$

where $D = 6 \times 10^{-6}$ cm²/s $A_E = 0.63$ cm²

$n = 4$ eq/mol $\delta = 0.002$ cm

<u>Excess Power Due to Oxygen Reduction</u>

$P_X = E_H I_L = (1.527\ V)(0.001\ A) = 1.5$ mW

for $\delta = 0.01$ cm $I_L = 0.0002$ A, $P_X = 0.3$ mW

for $\delta = 0.001$ cm, $I_L = 0.002$ A, $P_X = 3.0$ mW

PALLADIUM-BORON MATERIAL
PREPARED BY DR. M.A. IMAM, NAVAL RESEARCH LABORATORY

Excess heat produced in 7 out of 8 experiments at China Lake

Excess heat produced in NHE (Japan) experiment

Materials contained 0.25 to 0.75 weight % boron

Boron removes oxygen contamination in palladium

Boron hardens palladium material
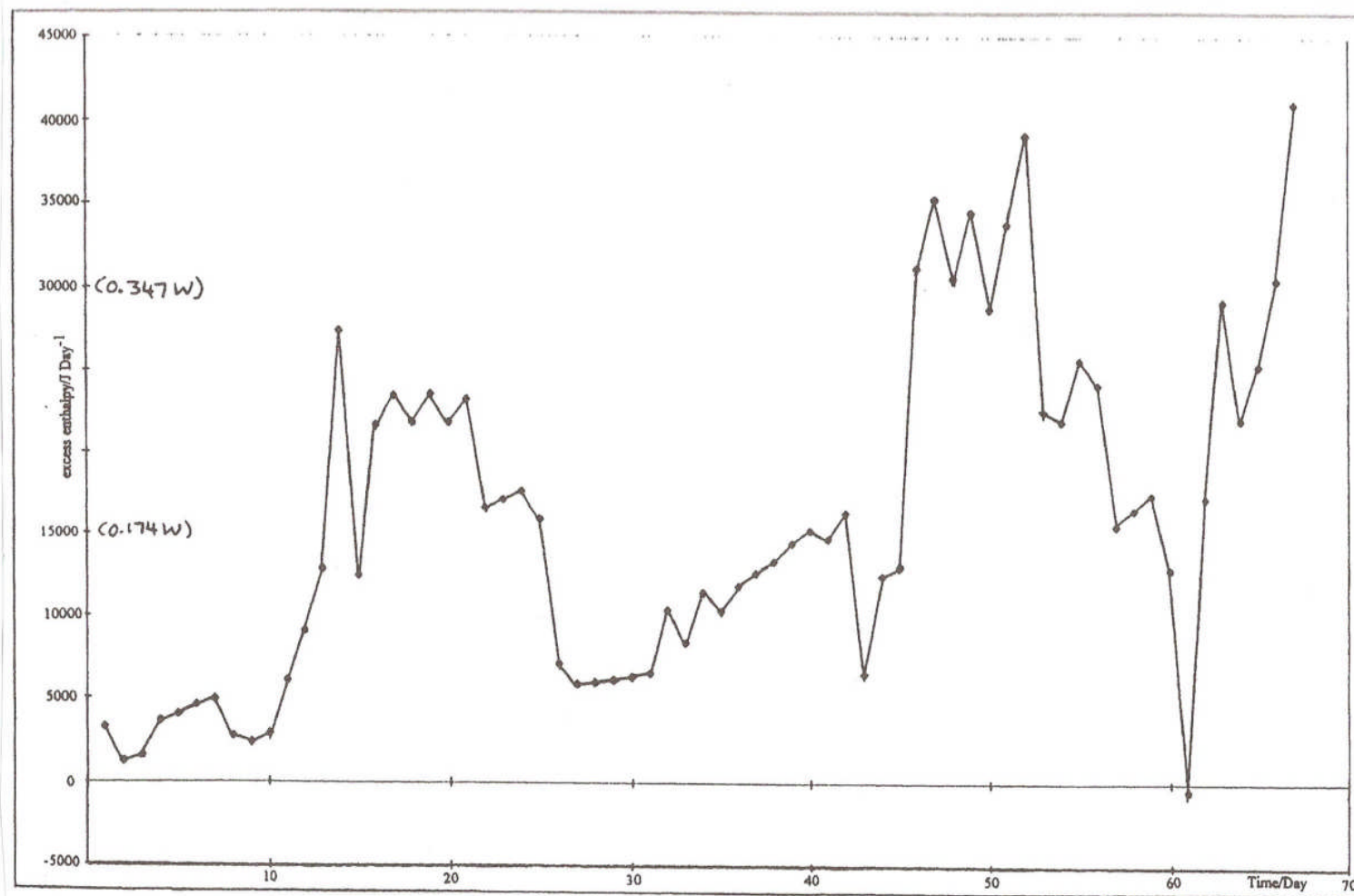
Boron resides in grain boundaries of palladium

<u>U.S. Patent</u>

"Palladium-Boron Alloys for Excess Enthalpy Production"
   M.H. Miles and M. Ashraf Imam
   U.S. Patent No. 6,764,561, June 20, 2004

Pd-B RESULTS
NHE/JAPAN

CALORIMETRIC EQUATIONS AND CALCULATIONS
(Further Information)

SEE:

1. Miles, M.H., Fleischmann, M. and Imam, M.A. (2001). Naval Research Laboratory Report Number NRL/MR/6320-01-8526, March 26, 2001.

2. Szpak, S. and Mosier-Boss, P.A. (2002). SPAWAR Systems Center Technical Report Number 1862, Volume 2, San Diego, CA.

3. Fleischmann, M. and Miles, M.H. (2006). In "Condensed Matter Nuclear Science", pp. 247-268, P.L. Hagelstein and S.R. Chubb, Editors, World Scientific, New Jersey, ISBN No. 981-256-564-7.

4. Fleischmann, M. and Miles M.H. (2006). Manuscript No. JP058292J submitted to *J. Phys. Chem.* Note: Editor George C. Schatz rejected this manuscript and ruled that the two reviewers did not need to respond to the detailed rebuttal by the authors to the reviewers comments.

SUMMARY

- **Correct Equations Yield High Calorimetric Accuracy**

- **Backward Integration of Data Sets Yields Best Results**

- **Excess Power Measurable to ±0.1 mW**

- **Reduction of Oxygen Measurable at 1.1 mW in Pt/D_2O system**

- **Recombination Effects are Very Small (1.1 mW)**

- **Pd-B Material Yields Large Excess Power Effects (50 to 500 mW)**

FURTHER INFORMATION / QUESTIONS

Further Information

See: "Condensed Matter Nuclear Science",
Proceedings of ICCF-10, P.J. Hagelstein and S.R.
   Chubb, Editors,
World Scientific, New Jersey ISBN 981-256-564-7, 2006,
   pp. 247-268.

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