The Fleischmann-Pons Calorimetric Methods And Equations

Melvin H. Miles

Department of Chemistry, University of La Verne

La Verne, California, USA 91750

(mmiles@laverne.edu)

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Short Cold Fusion Review

- ❖ **Martin Fleischmann Had Remarkable Skills in Calorimetry and Mathematical Modelling**
- ❖ **Vastly Inferior Calorimetric Experiments by CalTech, MIT and Harwell Blocked Scientific Acceptance**
- ❖ **A Great Scientific Discovery Became A Scientific Tragedy**
- ❖ **Many Cold Fusion Scientists Suffered Career Damage**

Stigmatizing of Cold Fusion Research For 27 years
Is The Real Scientific Fiasco

Fleischmann and Pons Were Correct

- ➢ **Sometimes Scientists Get It Wrong, But Important Discoveries Are Also Often Rejected For Many Years (Galileo, Joule, Semmelweis, Arrhenius, Wegener And Many Others)**

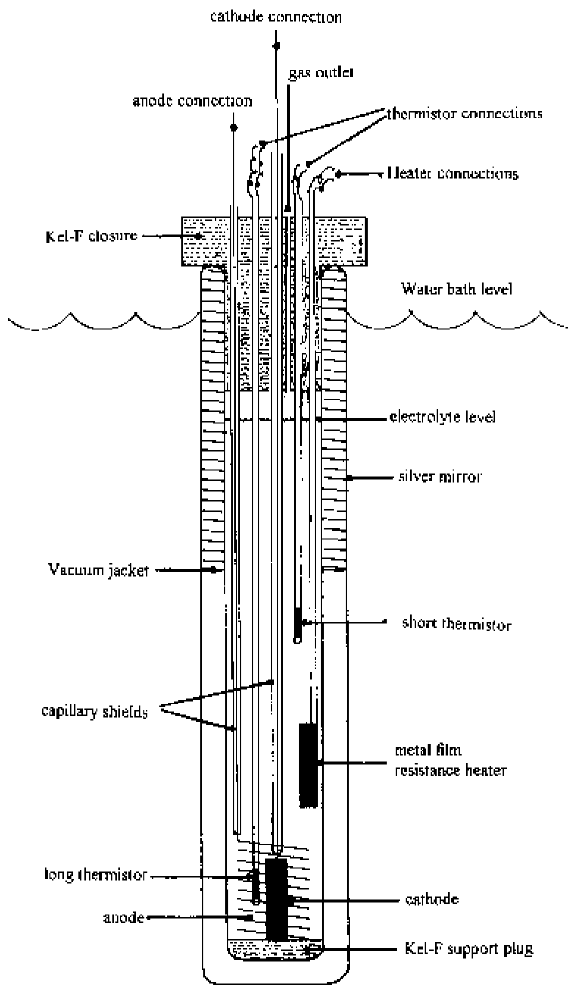
Why Is The Fleischmann-Pons Calorimetry Important Today? (27 Years Later)

- **Major Topic Of 1989 Cold Fusion Controversy**
  (Field Has Never Recovered From CalTech, MIT, Harwell Rejection)
- **Poorly Understood By Most Scientists**
  (Even Cold Fusion Researchers)
- **Very Accurate When Correctly Applied**
  (Error About ±0.01% or ±0.1 mW)
- **Possible Application For Many Other Electrochemical Studies**

Martin Fleischman (1927 – 2012)

- **Outstanding skills In Mathematics And Modelling.**
- **Mathematical Equations Required In This Presentation.**

Fleischmann-Pons Dewar Cell



Inside Diameter = 2.5 cm
Height = 25.0 cm
Silvered = 8.0 cm (Top)
Electrolyte Volume = 90.0 cm^3

Advantages Of The Fleischmann-Pons Calorimetry (Dewar Cell, Isoperibolic)

- **Provides Direct View Inside Cell**
- **No Memory Effect / Heat Transferred By Radiation Photons**
- **Stefen-Boltzmann Constant Provides Estimate Of Radiative Heat Transfer Co-efficient**

$$k_R \approx (5.670373\text{x}10^{-8}\ \text{Wm}^{-2}\ \text{K}^{-4})(\text{cell surface area, m}^2)$$

- **Wide Dynamic Range for Cell Temperature and Cell Voltage (100°C, 10 V)**
- **Small Diameter Cell Provides Good Mixing**

(NHE Cell 2.5 x 25 cm)

- **Inherent Safety / Self Purifying (D_2, O_2 Exit Cell) ,**
- **Relatively Low Cost**
- **High Accuracy / Computer Data Acquisition**

(Measurements Every 300 seconds)

Notes: Fleischmann-Pons Considered Various Calorimetric Methods

Isoperibolic Calorimetry With Dewar Cell Was Selected As Most Accurate

Temperature Measurements Limit Calorimetry Accuracy

$$P_x = f\,(T_{cell}, T_b, I_{cell}, E_{cell})$$

Fleischmann-Pons	T ± 0.001 K	(Calibrated thermistors)
Miles	T ± 0.01 K	(Calibrated thermistors)
Cal Tech	T ± 0.03 K	
MIT, Harwell	T ± 0.1 K	

For $T_{cell} - T_b$ = 10.000 K and 1000 mV Input

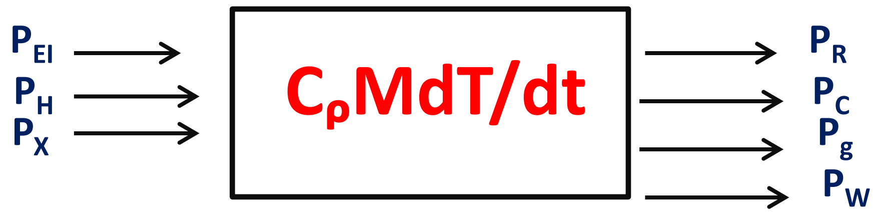
F/P Error	= ±0.001/10 = ±0.0001	(± 0.01%	, ± 0.1 mW)
Miles Error	= ±0.01/10= ±0.001	(± 0.1%	, ± 1 mW)
MIT Error	= ±0.1/10= ± 0.01	(± 1%	, ± 10 mW)

Mathematical Modelling And Calorimetric Equations

Poorly Understood / Major Roadblock

MODEL

Cell



$$C_\rho MdT/dt = P_{EI} + P_H + P_X + P_R + P_C + P_g + P_W$$

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

$P_R = -k_R f(T)$ where $f(T) = T^4 - T_b^4$

$P_C = -k_C (T - T_b)$

$C'_P = C_{p'}(D_2O) + C_{\rho'}(\text{glass}) + C_p(\text{metals}) = C_\rho M\ (JK^{-1})$

Cell Electrochemistry

$$D_2O_{(l)} \rightarrow D_{2(g)} + \tfrac{1}{2} O_{2(g)}$$

$$C_\rho M = C_\rho M^\circ (1 - \alpha t)$$

$$k_R = k^\circ_R (1 - \beta t)$$

No Steady State Cell Temperature

(k_R and $C_\rho M$ Change With Time)

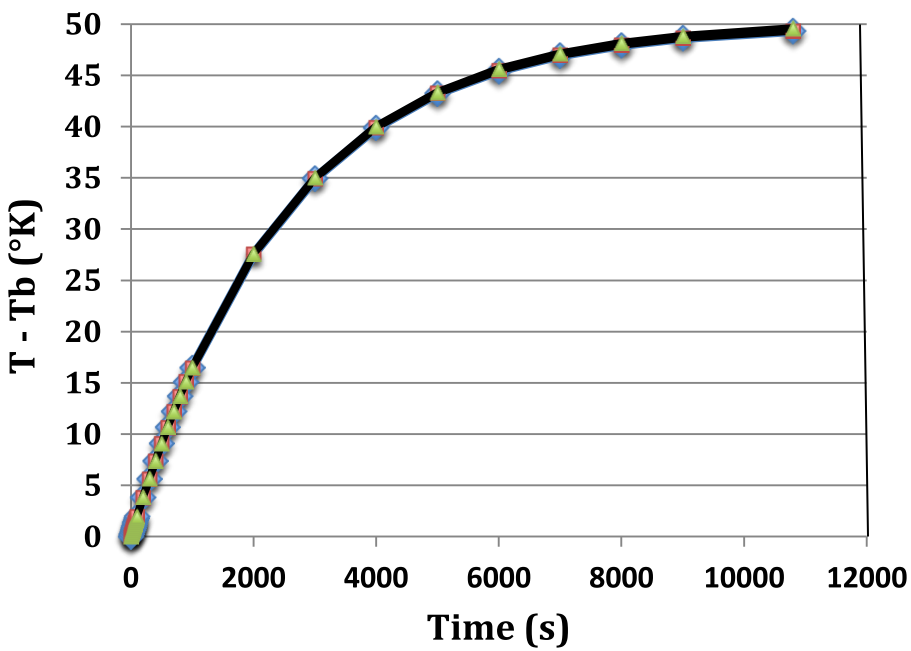


Figure 1. Cell temperature versus time for the first three hours of cell operation.

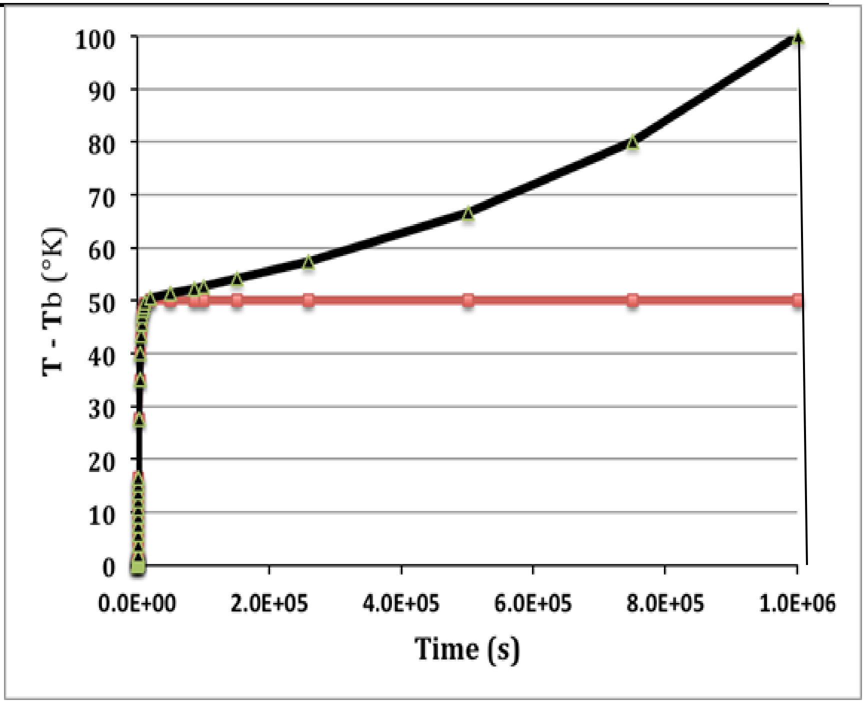


Figure 2. Cell temperature versus time for the first eleven days of cell operation.

$$\Delta T = T - T_b = \alpha t \quad (\text{ for } t < 1000 \text{ s})$$

$$\alpha = [(E - E_H)\, I + P_X] / C_P M^\circ$$

See Melvin H. Miles, J. Condensed Mater Nucl. Sci., Vol. 19, 2016

Lower Bound Radiative Heat Transfer Coefficient, k'_R

(Assumes $P_X = 0$)

$$C_pMdT/dt = P_{EI}+P_H+P_X - k_R\, f(T) + P_C + P_g + P_W \quad (1)$$

$$C_pMdT/dt = P_{EI} + P_H + 0 - k'_R\, f(T) + P_C + P_g + P_W \quad (2)$$

Eq. 1 – Eq. 2] $\quad 0 = P_X - k_R\, f(T) + k'_R\, f(T)$

Therefore $\boxed{P_X = (k_R - k'_R) f(T)}$ where $k_R \geq k'_R$ and $f(T) = T^4 - T_b^4$

Similarly $P_X = (k_C - k'_C)(T - T_b)$ for Heat Conduction Calorimetry

$$\boxed{k'_R = (P_{EI} + P_H + P_C + P_g + P_W - C_pMdt/dt) / f(T)}$$

- Allows calorimetry while determining value for k_R

See M. Fleischmann and S. Pons, Physics Letters A, Vol. 176, pp. 118-129, 1993

$(k'_R)_{11} = (P_{EI} + P_g - C_pMdT/dt) / f(T)$ (Eq. 2, p. 4)

Information Provided by Lower Bound Heat Transfer Coefficient

- ❑ Enthalpy Produced By Palladium Loading
- ❑ Information On D-Loading Behavior
- ❑ Excess Power Production

$P_X = (k_R - k'_R)\, f(T)$ $\Rightarrow$ $k'_R = k_R - P_X / f(T)$ where $f(T) = T^4 - T_b^4$

Exothermic Deuterium Loading: $(x/2)\, D_2 + Pd \longrightarrow PdD_x + \text{Heat} \quad (P_X > 0)$

Initially small f(T) yields $k'_R < 0$ (Negative)

Experimental Results

$Pt/D_2O \Rightarrow P_X = 0$ and $k'_R = k_R$ everywhere

$Pd/H_2O \Rightarrow$ Initial $P_X > 0$, $k'_R < 0$, Later $k'_R = k_R$

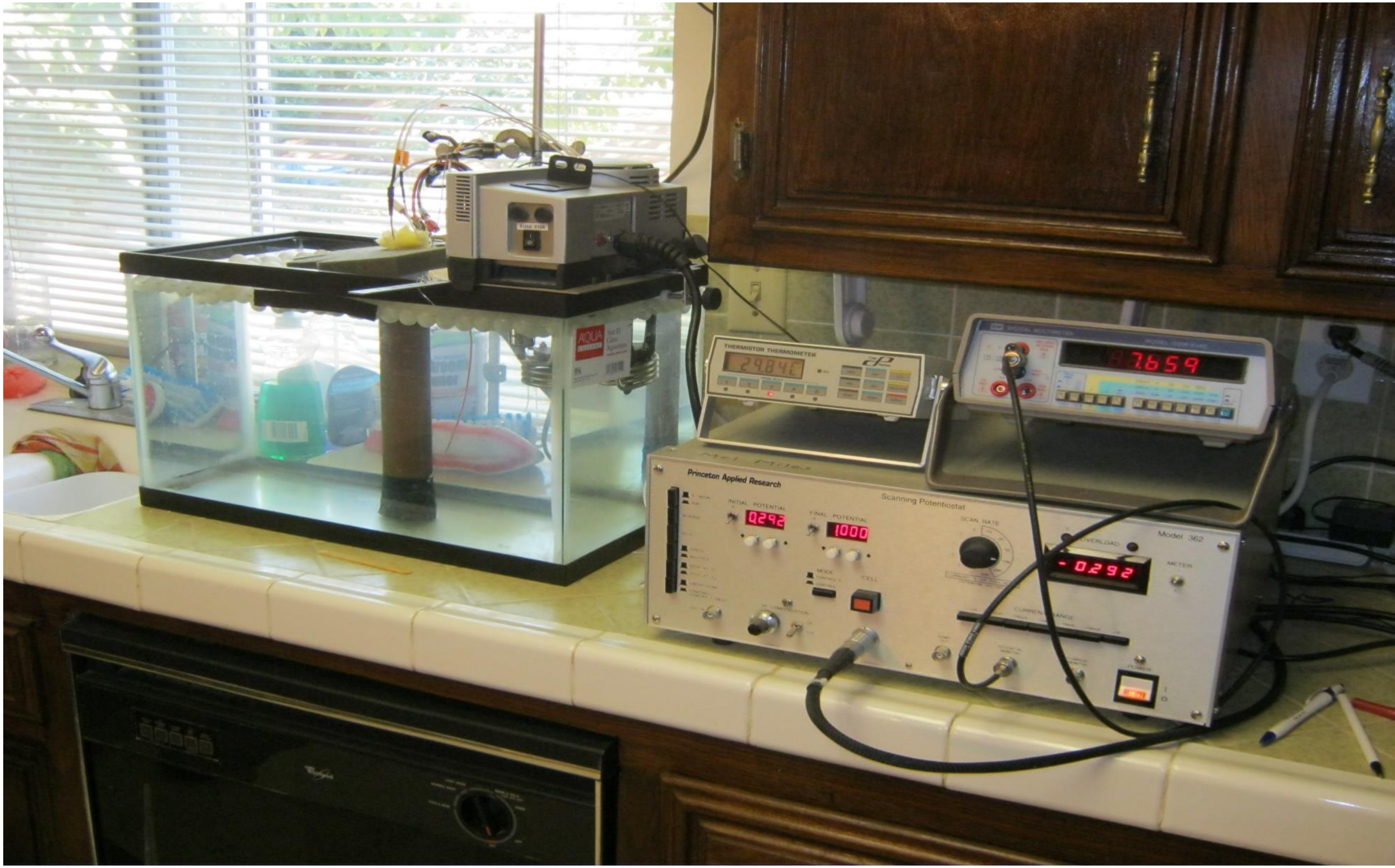
$Pd/D_2O \Rightarrow$ Initial $P_X > 0$, $k'_R < 0$, Later $k'_R < k_R$

See M. Fleischmann and S. Pons, Physics Letters A, Vol. 176, pp. 118-112, 1993

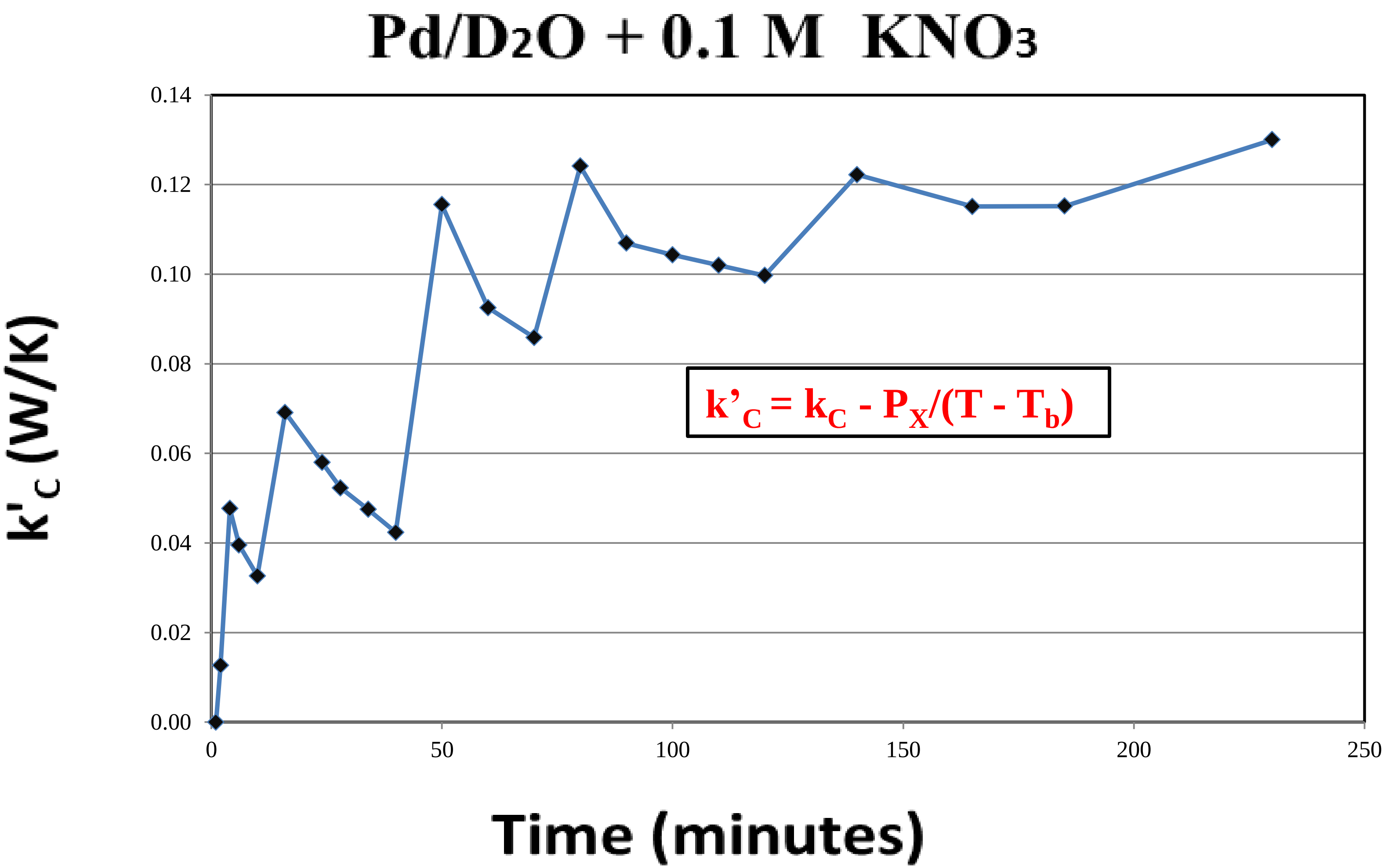
$$\Delta H = -\int_o^t P_X dt = -\int_o^t (k_R - k'_R)\, f(T) dt = -35.1 \text{ kJ/mol } D_2\ (PdD_{0.6})$$

My Recent Kitchen Experiment

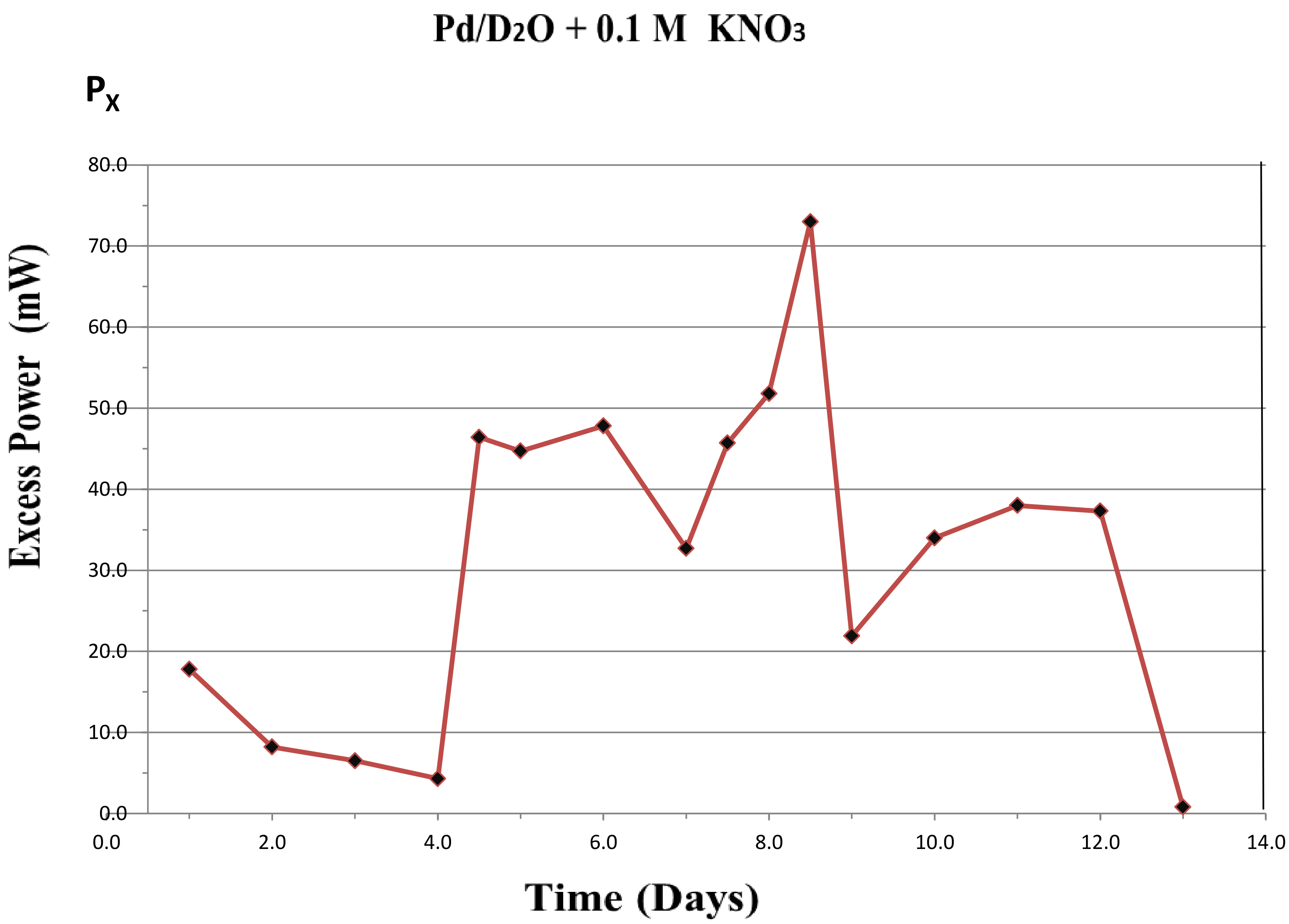
(July, 2016)



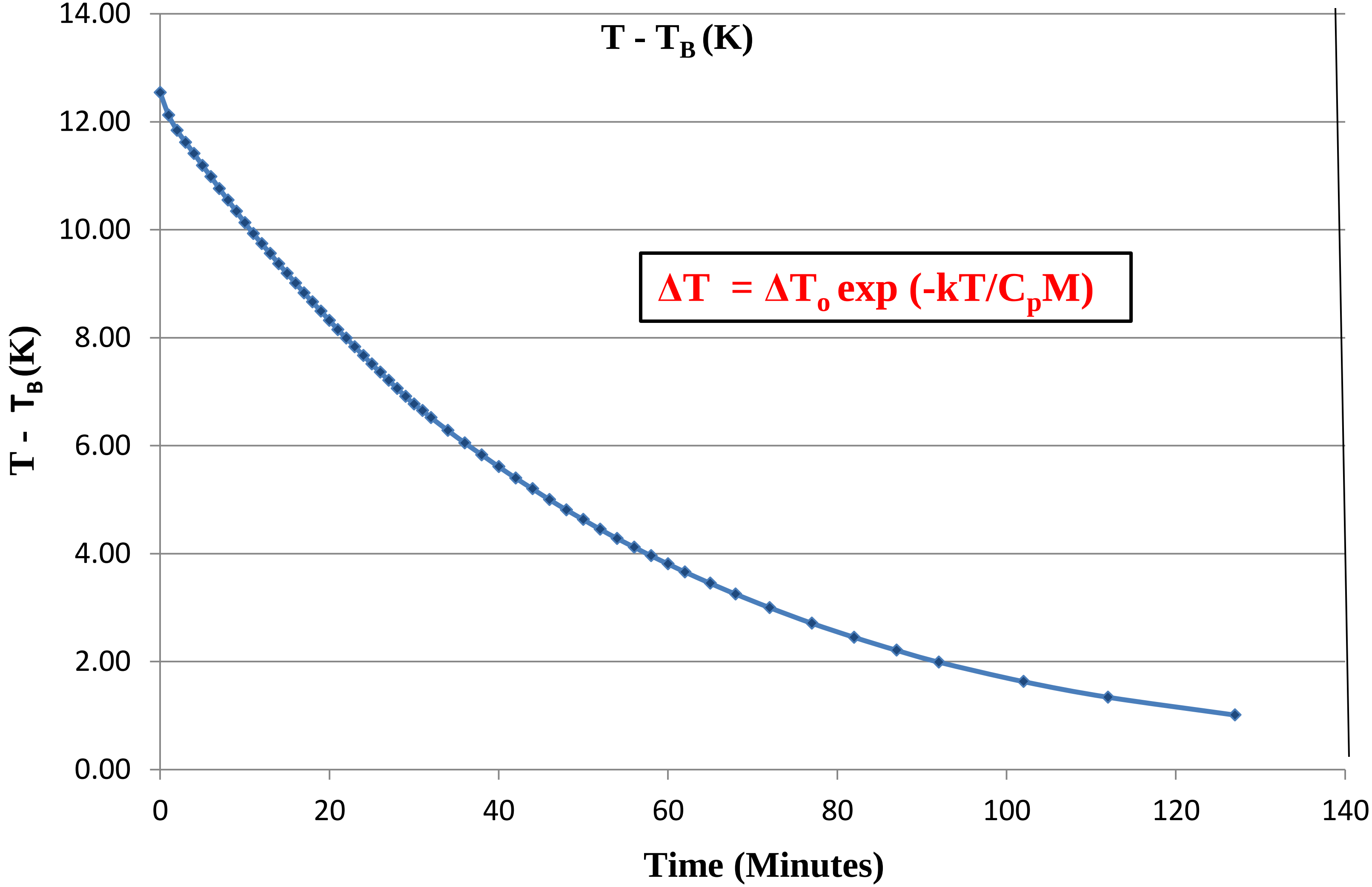
Example For Lower Bound k'_c



Excess Power Measurements



Experimental Cell Cooling At Zero Current
(Pd/D_2O + 0.1 M KNO_3)



Experimental Versus Theoretical Cooling Rates
Pd/D_2O + 0.1 M KNO_3

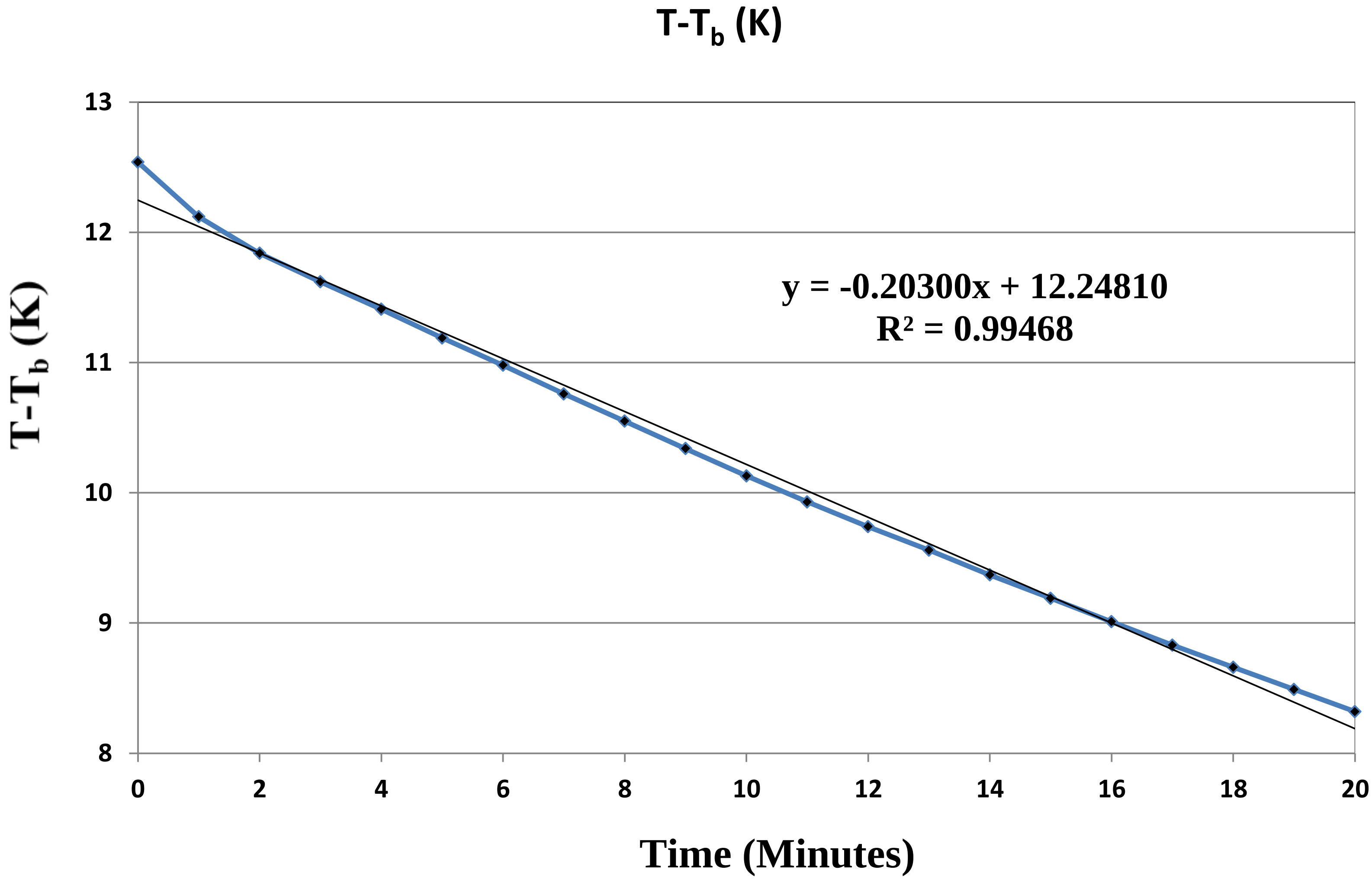
$$dT/dt = -(k/C_pM)\Delta T + P_X/C_pM - P'_X/C_pM$$

where k = 0.1348 W/K and C_pM = 430 J/K

Time (minutes)	ΔT (K)	Exp. (K/min)	Theoretical (K)
2	11.84	-0.28	-0.223
5	11.19	-0.22	-0.211
10	10.31	-0.21	-0.191
15	9.19	-0.18	-0.173
20	8.32	-0.17	-0.156
30	6.77	-0.14	-0.127
40	5.61	-0.11	-0.106
50	4.63	-0.09	-0.087

Initial Cooling For Pd/D_2O + 0.1 M KNO_3

$\Delta T = \Delta T_o \exp(-kt/C_pM) \approx \Delta T_o (1 - kt/C_pM)$



Cell Cooling at End of Experiment
(I = 0)

- Evidence For Heat-After-Death
- Ratio of $k_R / C_\rho M$ or $k_C / C_\rho M$

Conductive Heat Transfer

$$C_\rho M dT/dt = - k_C (T - T_b)$$

$$\ln(T_o - T_b) / (T - T_b) = (k_C / C_\rho M)t$$

$$\Delta T = \Delta T_o \exp(- k_C t / C_\rho M)$$

Radiative Heat Transfer

$$C_\rho M dT/dt = - k_R (T^4 - T_b^4)$$

$$\ln(T_o - T_b) / (T - T_b) - \ln(T_o + T_b) / (T + T_b) + 2[\tan^{-1}(T / T_b) - \tan^{-1}(T_o / T_b)] = 4 T_b^3 k_R t / C_\rho M = (k'_C / C_\rho M)t$$

- ✓ Straight-Line Form: $y = mx$
- ✓ Same Slope if $k_C = k'_C$ and same $C_\rho M$ value

Expressions For Radiative Power

$$\Delta T = T - T_b \text{ or } \boxed{T = T_b + \Delta T}$$

$$P_R = - k_R \ (T^4 - T_b^4) = - k_R \ [(T_b + \Delta T)^4 - T_b^4]$$

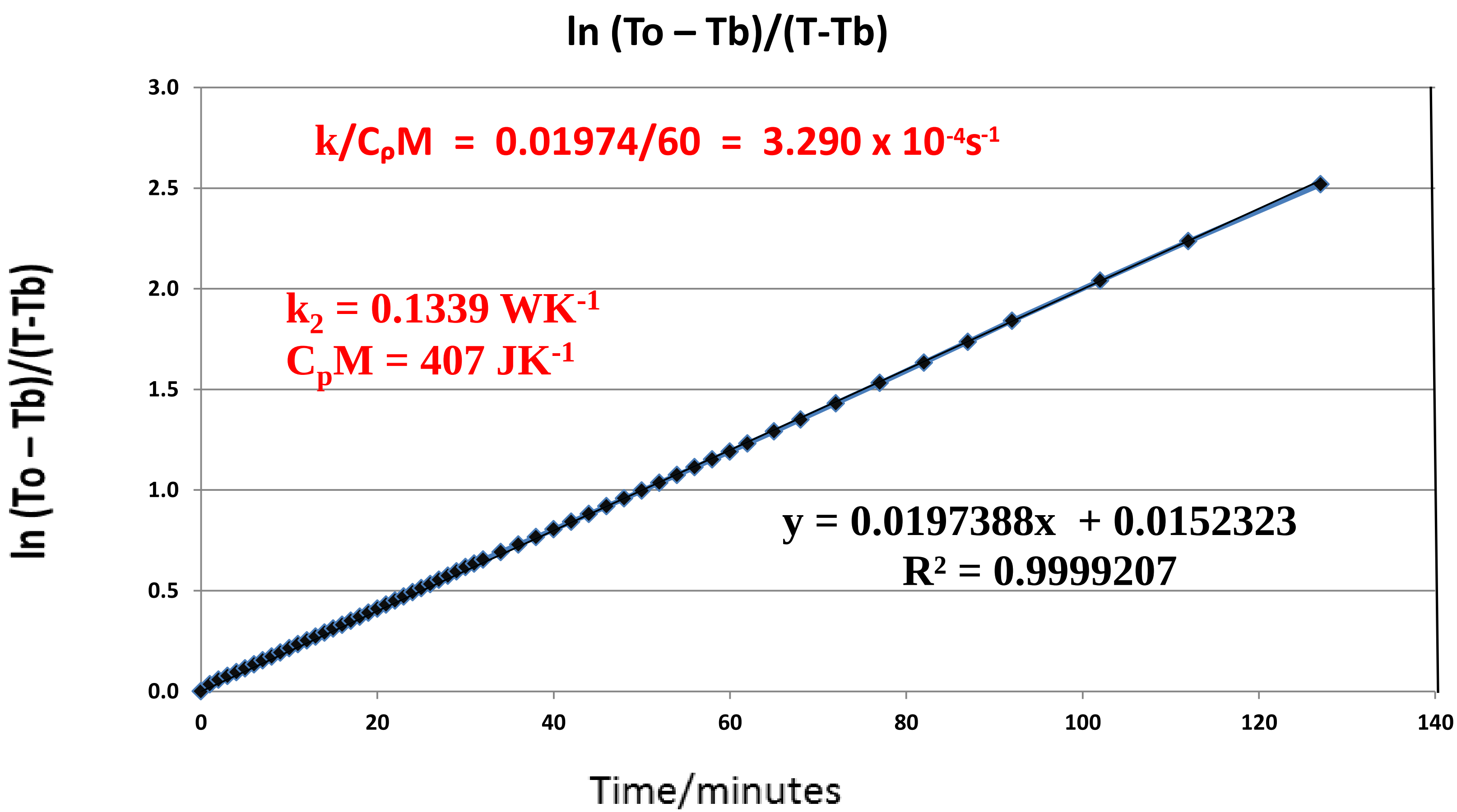
$$P_R = - k_R (T_b^4 + 4T_b^3 \Delta T + 6 T_b^2 \Delta 4T_b \Delta T^3 + \Delta T^4 - T_b^4)$$

$$\boxed{P_R = - k_R [4 T_b^3 \Delta T + 6 T_b^2 \Delta T^2 + 4T_b \Delta T^3 + \Delta T^4]} \qquad \text{(Exact)}$$

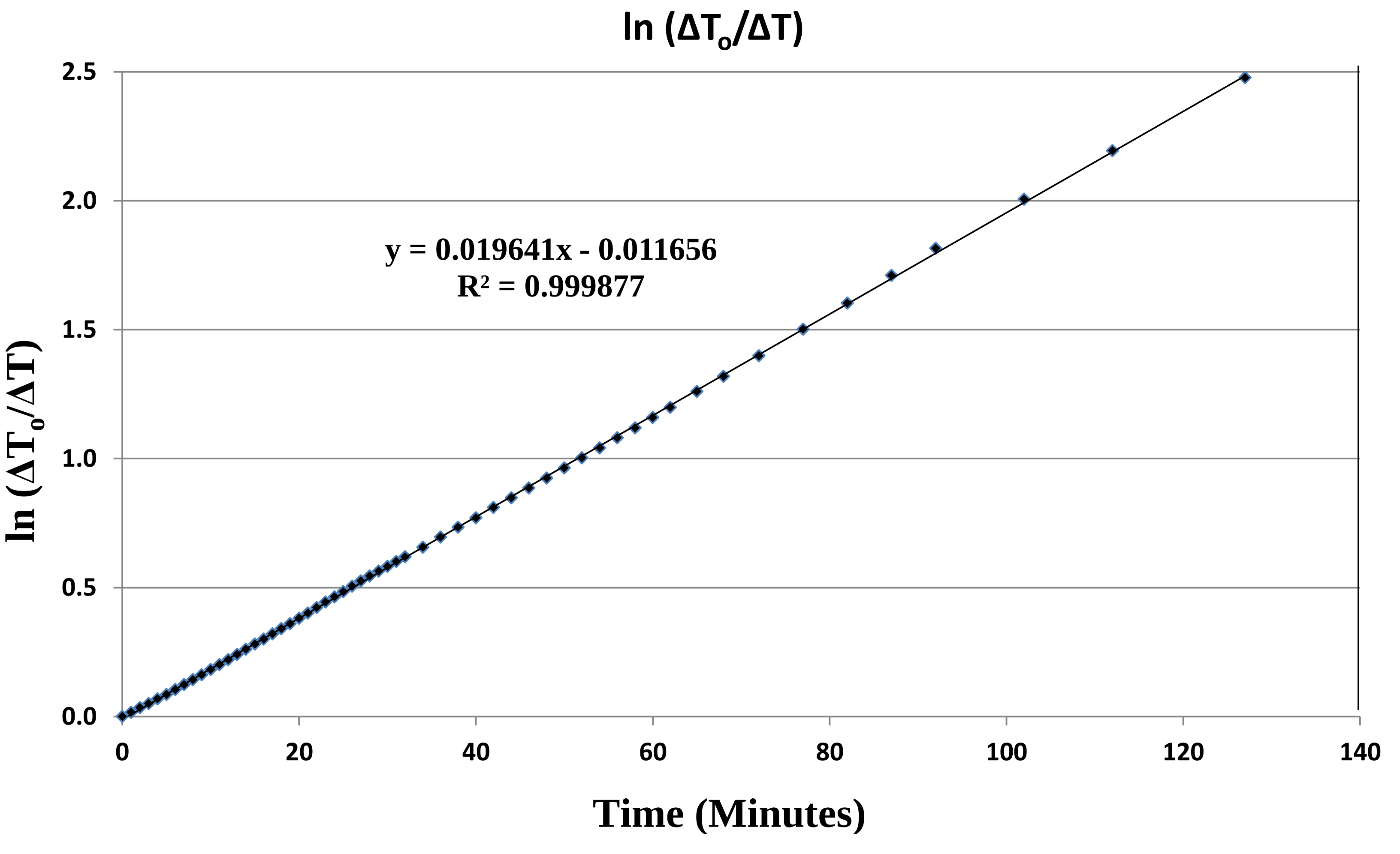
$$P_R \approx - 4 T_b^3 k_R \Delta T = - k'_C \Delta T \qquad \text{(Approximate)}$$

where $k'_C = 4 T_b^3 k_R \Delta T$

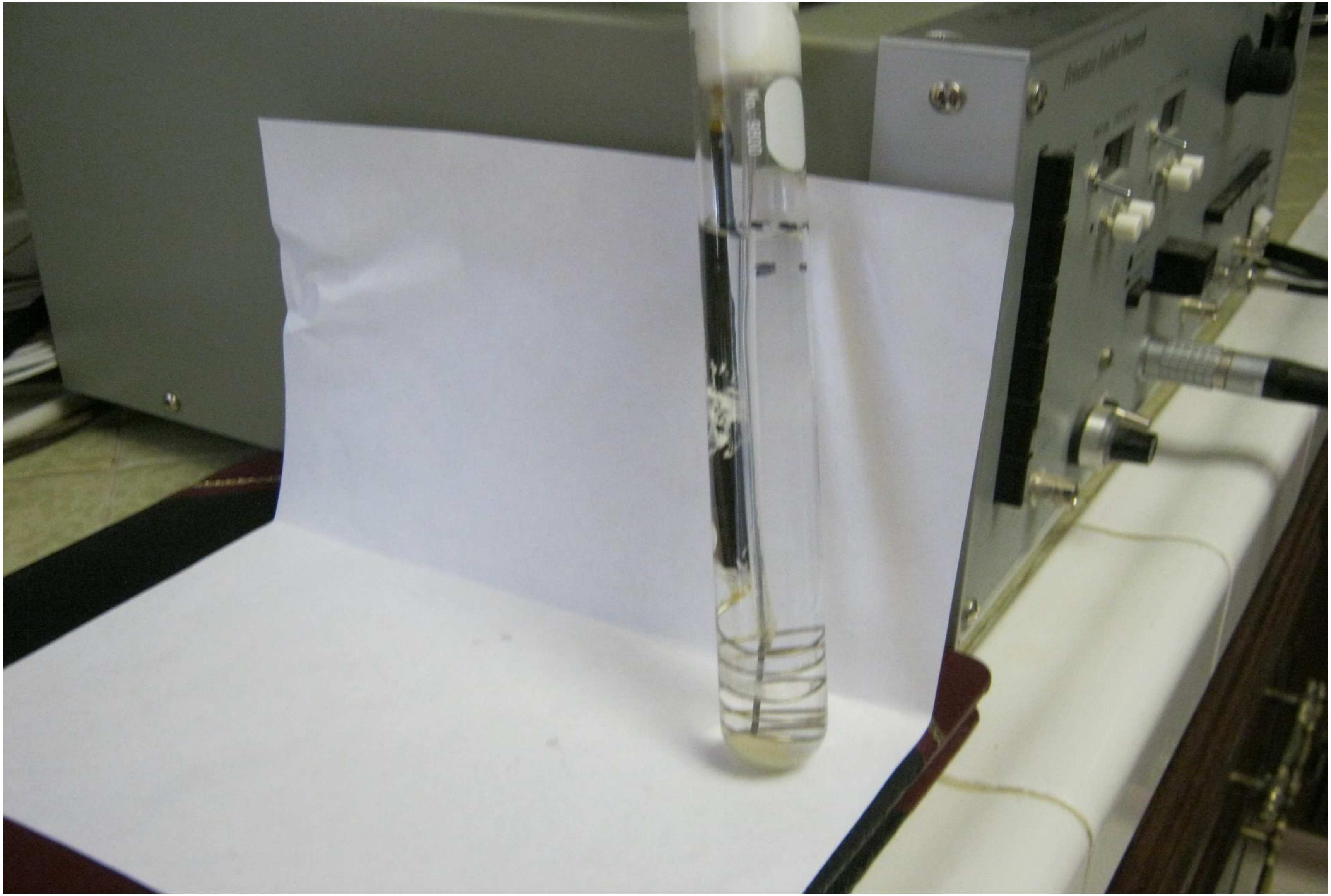
Cooling Curve For Pd/D_2O + 0.1 M KNO_3
(Heat Transfer By Conduction)



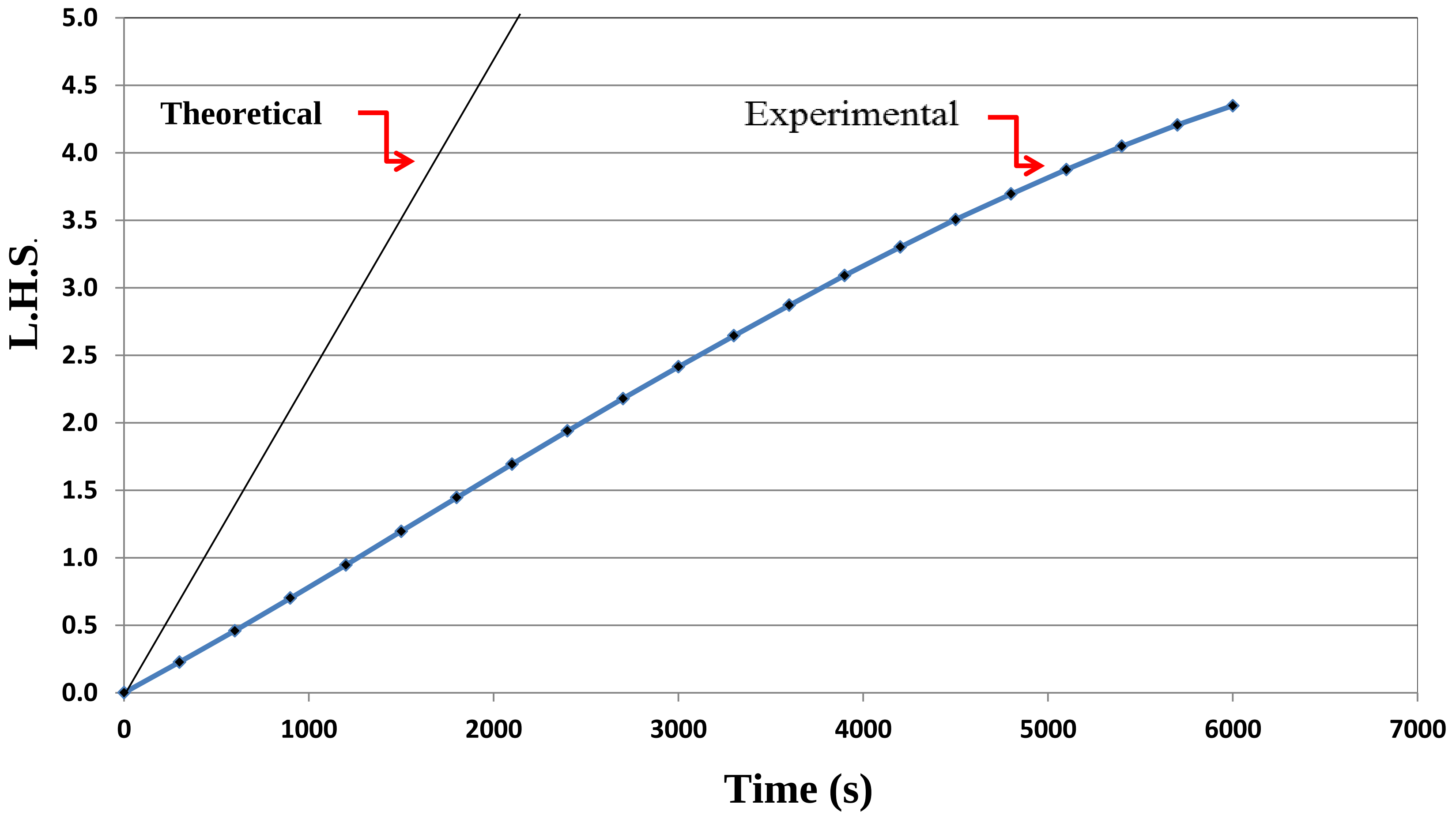
Cooling Curve Using Second Thermister
$(Pd/D_2O + 0.1\ M\ KNO_3)$



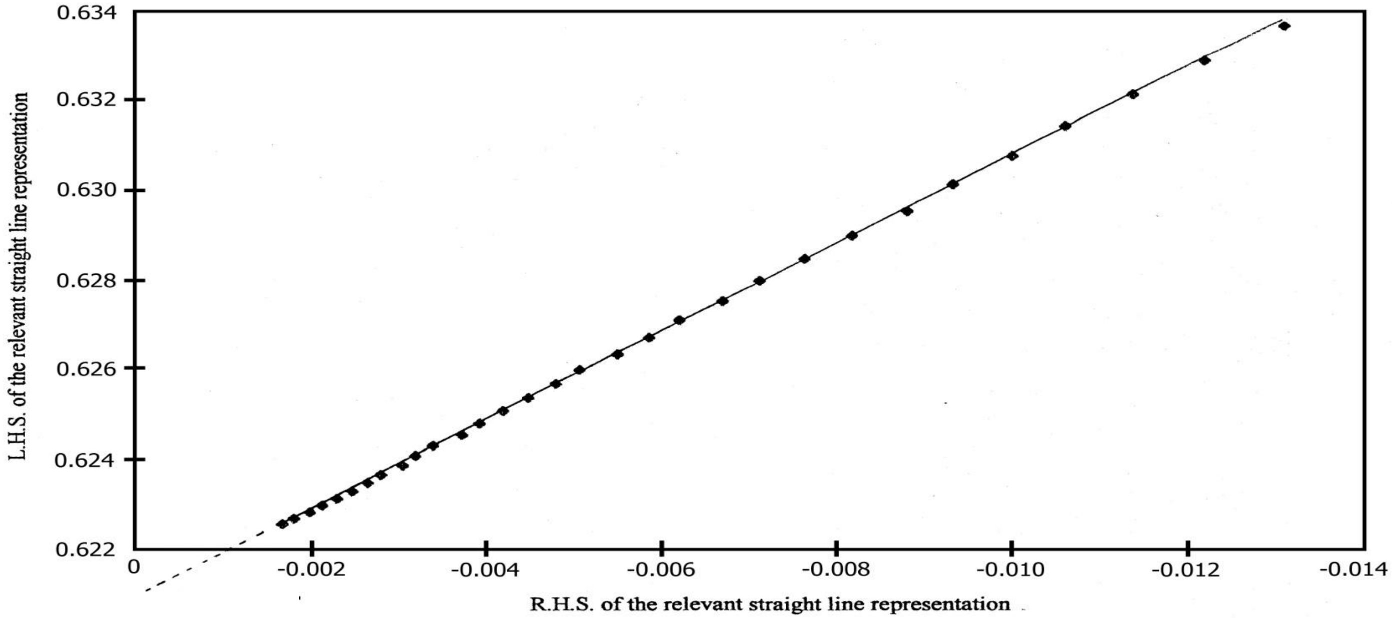
Electrochemical Cell Following Experiment



Cooling Curve For Pd-B Experiment With Excess Power (Dewar Cell)



Fleischmann's Straight Line Method (Dewar Calorimetry)
(y = mx +b)



γ – intercept yields $k_R = 0.62085 \times 10^{-9}\ WK^{-4}$ 5 significant figures

Slope = $C_\rho M/C_\rho M'$ yields $C_\rho M) = 341.1\ JK^{-1}$

- Platinum / D_2O Control
- Assumes P_X is Zero or Constant
- Uses Backward Integration of Calorimetric Data (t_2, t)
- t_2 is midpoint of two-day cycle
- t is near beginning of cycle

Derivation of Fleischmann's Straight Line Method

$$C_\rho MdT/dt = P_{EI} + P_H + P_X + P_R + P_C + P_g + P_W$$

$C_\rho MdT/dt = -k_R\, f(T) + P_{net} + P_X$

where $P_{net} = P_{EI} + P_H + P_g + P_W$ and $P_R >> P_C$

$C_\rho MdT = -k_R\, f(T)dt + P_{net}\, dt + P_X dt$

$(P_{net} + P_x)dt = C_\rho MdT + k_R\, f(T)dt$

Algebraic Rearrangements

$\int(P_{net} + P_X)dt / \int f(T)dt = C_\rho M\int dT/\int f(T)dT + k_R$

$y = C_\rho M\, x + k_R$

Let $x = x' / C_\rho M'$

$y = C_\rho Mx' + k_R$

Integration and Substitution

Integrate / Multiply by 10^9

Note

$$10^9\,[y] = 10^9\, C_\rho M\,[X']/C_\rho M' + 10^9\, K_R$$

$[y]$, $[x']$ and k_R
Have units of WK^{-4}

y – Intercept = $10^9\, k_R$
Slope = CpM/CpM' ≈ 1

Combining Radiation and Conduction Terms

$(P_R >> P_C)$

$$P_R + P_C = - k_R (T^4 - T_b^4) - k_C (T - T_b)$$

Let $P'_R = P_R + P_C = - (k'_R)(T^4 - T_b^4) = - k_R (T^4 - T_b^4) - k_C (T - T_b)$

$$(k'_R) = k_R + k_C (T - T_b) / (T^4 - T_b^4)$$

- ❑ Small Increase in k_R Accounts for Heat Conduction Terms.

Power Term For Temperature Change Of Calorimeter P_{calor}

$$P_{calor} = C_\rho \, d/dt\,[M(T-T_b)] = C_\rho M \, d/dt\,(T-T_b) + C_\rho\,(T-T_b)\, dM/dt$$

where $M = M° - (1+\beta)\,\gamma\, It/2F$

For T_b = Constant And γ = 1.00

$$P_{calor} = C_\rho M \, dT/dt - C_\rho\,(T-T_b)(1+\beta)\, I/2F$$

$$\boxed{P_{calor} \approx C_\rho M \, dT/dt}$$

Power Term For Rate of Work (P_w)

$$0.5\ D_2O \rightarrow 0.5\ D_2 + 0.25\ O_2$$

per Faraday, F

$W = - P\Delta V = - \Delta nRT$

$\Delta n = 0.75\ (I/F)$ in moles/s

$$P_W = - 0.75\ (I/F)\ RT$$

If D_2O vapor is also considered, then

$$P_W = - 0.75\ (1 + P')(I/F)\ RT$$

where $P' = P / (P^* - P)$

__Note__

$E_H = - \Delta H / ZF$ __Does Not Account For Work__

$H = U + PV$ (Definition)

$(\Delta H)_\rho = \Delta U + P\Delta V$ where $\Delta U = q - P\Delta V$ (1^{st} Law)

$(\Delta H)_\rho = (q - P\Delta V) + P\Delta V = q$ (Heat)

Power Term For Escaping Gases (P_g)
(D_2, O_2, D_2O vapor)

$$0.5\ D_2O \rightarrow 0.5\ D_2 + 0.25\ O_2$$

Per Faraday (F)

$$P_g = -(I/F)[0.5\ C_{P,D2} + 0.25\ C_{P,O2} + 0.75\ P'\ C_{P,D2O}]\ \Delta T - 0.75\ (I/F)\ P'\ L$$

where $P' = P/(P^* - P)$

$$P^* = P_{D2} + P_{O2} + P_{D2O} \approx P_{atm}$$

Notes: P_g will be small for $T < 70°C$

Atmospheric Pressure needed for calculations of P_g

F – P Approximation (1993)

$$P'_g = -0.75\ (I/F)\ P'[C_{P,D2O\ (g)} - C_{p,D20(l)}]\ [\Delta T + L]$$

Note: P'_g less negative than P_g

Factors For Attaining The Fleischmann-Pons Calorimetric Accuracy

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- **Accurate Cell and Bath Temperature Measurements (±0.001 K)**
- **Data Averaging (Data collected every 300 s)**
- $\bar{k}_R$ 11–point Average , $\bar{\bar{k}}_R$ 6 – point Average of $\bar{k}_R$
- **Numerical Integration of Calorimetric Data**
- **Straight-Line Method for obtaining k_R and $C_\rho M$**
- **Use of Two-Day Cycles with Heater Application (12 hours)**
- **Control of Room Temperature (± 1°C)**
- **Use of all Calorimetric Terms (P_{EI}, P_H, P_R, P_C, P_g, P_W)**
- **Measurements of Atmospheric Pressure Each Day For P_g Calculations**
- **Silver Coating of Top 30% of Dewar Calorimetric Cell (Minimizes Electrolyte Level Effect)**
- **Control of Electrolyte and Bath Levels**
- **Adequate Cell Current for Stirring / Small Cell Diameters**

Calorimetric Error of Only ±0.01% (±0.1 mW)

- Measure When Cold Fusion Effect First Begins

Summary

- F-P Dewar Calorimetry Is Most Accurate System Reported For Cold Fusion
  Error only ±0.01% (±0.1 mW)
- Accuracy of Temperature Measurements Determines Error Limit
- Calorimetric Design Offers Many Advantages
  (View Inside Cell, Wide Dynamic Range, Safety)
- Initial Period Provides Important Information
  D-Loading Behavior , Lower Bound k'_R or k'_C
- Numerical Integration Provides Accurate k_R and C_PM Values
- Important Information From Cell Cooling (I=0)
  (Heat-After-Death , k_R / C_PM Ratio)
- All Power Terms Should Be Considered (C_PMdT/dt, P_{EI}, P_H, P_R, P_C, P_g, P_W)
- Considerable Mathematical Equations Involved

For All Slides, Contact: melmiles1@juno.com
mmiles@laverne.edu

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  Kalynn Larson