NEW APPROACHES TO ISOPERIBOLIC CALORIMETRY

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Relative inexpensive isoperibolic calorimeters have been designed and constructed with the goal of obtaining a constant heat transfer coefficient that is insensitive to normal changes in the electrolyte level. The first four prototypes were constructed from copper tubing and used different insulating materials. The outer copper cylinder has a 5.1 cm (2.0 inch) diameter and a 28 cm length. The inner copper cylinder (3.2 cm x 20 cm) is completely separated from the outer cylinder by the insulating material. The glass electrochemical cell (2.5 cm x 20 cm) positioned inside the inner copper cylinder contains 50 mL of electrolyte and has two thermistors positioned on opposite sides of the outer wall of the glass cell. Thermal contact between the glass cell and the inner copper tube is provided by Mobil 1 (5W-30W) motor oil (35 mL) as a heat conducting fluid. This calorimetric design provides for high cell operating temperatures.

Preliminary tests on these prototype calorimeters show excellent stability for the cell temperature measurements (± 0.002¡C), stable heat transfer coefficients during electrolysis, and a precision of ±5 mW (±0.6%) in power measurements up to 800 mW of input power. It is expected that the goal for a precision of ±1 mW or better can be attained with these new approaches to isoperibolic calorimetry. The heat transfer coefficient (k_C) for Cell A is 0.164 W/K, the heat capacity (C_pM) is 450 J/K and the time constant is 40 minutes.

The modeling of these new isoperibolic calorimeters uses the equation $P_{calor} = P_{EI} + P_H + P_X + P_C + P_R + P_{gas} + P_W$ where these power terms have all been defined elsewhere [1,2]. Assuming $P_H + P_X + P_R = 0$ in control experiments, this equation can be rearranged to yield $k_C \Delta T = P_T$ where $P_T = (E-E_H)I + P_{gas} + P_W - P_{calor}$. For conditions where $(E - E_H)I >> (P_{gas} + P_W - P_{calor})$, then $k_C \Delta T = (E - E_H)I$. For the most accurate results, all of the calorimetric power terms should be included, averaging of the data sets is advised, and numerical integration of the calorimetric differential equation is necessary [1,2].

The first application of these new isoperibolic calorimeter designs is in progress for co-deposition systems. Applications to the study of Pd-B and other alloy materials are also planned. Financial help is acknowledged by M.H.M. from an anonymous fund at the Denver Foundation via Dixie State College.

1. M.H. Miles and M. Fleischmann, "Accuracy of Isoperibolic Calorimetry Used in a Cold Fusion Control Experiment", in *Low-Energy Nuclear Reactions Sourcebook*, J. Marwan and S.B. Krivit, editors, ACS Symposium Series 998, pp. 153-171, 2008.
2. M.H. Miles and M. Fleischmann, "Isoperibolic Calorimetric Measurements of the Fleishmann-Pons Effect", ICCF-14, Washington, D.C. August 10 – 15, 2008.

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Desired Features of Isoperibolic Calorimeters

- ❖ **Simple Construction / Low Costs**
- ❖ **Wide Dynamic Range**
  - – **Cell Temperature (20°C → Boiling)**
  - – **Cell Input Power (0 → 10 Watts)**
- ❖ **Required k_c = 0.13 W/K or k_R = 0.83 x 10^{-9} W/K^4**
- ❖ **Self-Purifying (H Removed Preferentially to D)**
- ❖ **Inherent Safety (D_2, O_2 Exit Cell)**
- ❖ **Direct Visual Observation Inside Cell (Dewar Cell)**
- ❖ **High Accuracy (±1 mW, ±0.1%)**
- ❖ **Heat Transfer Mainly By Conduction or Radiation**
- ❖ **Stable Cell Constants Independent of Electrolyte Level**

Diagram of the Fleischmann-Pons Dewar Calorimeter ICARUS-1 TYPE

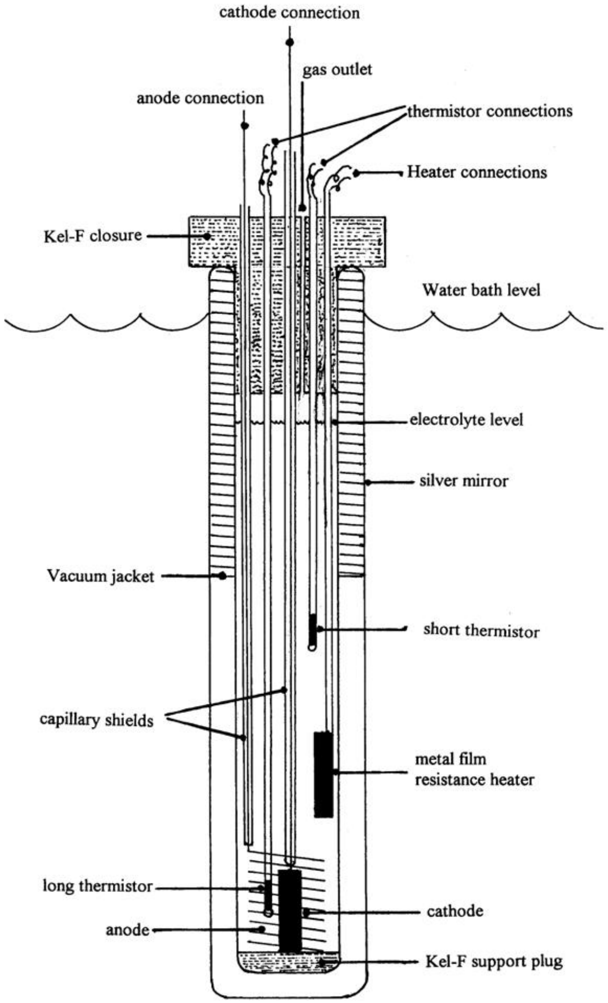


Diagram of the Fleischmann-Pons ICARUS-14 Calorimeter
(Never Constructed)

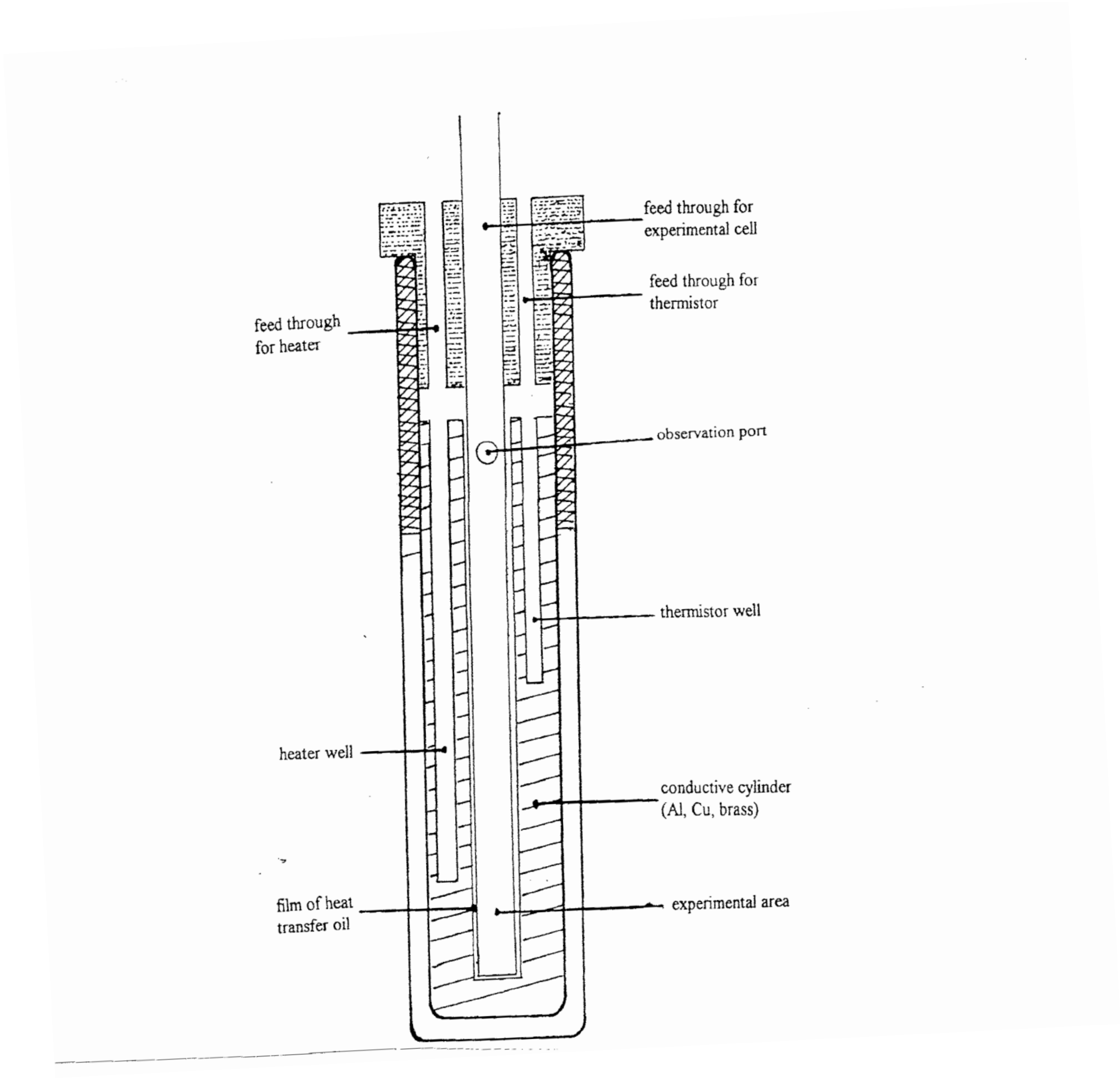


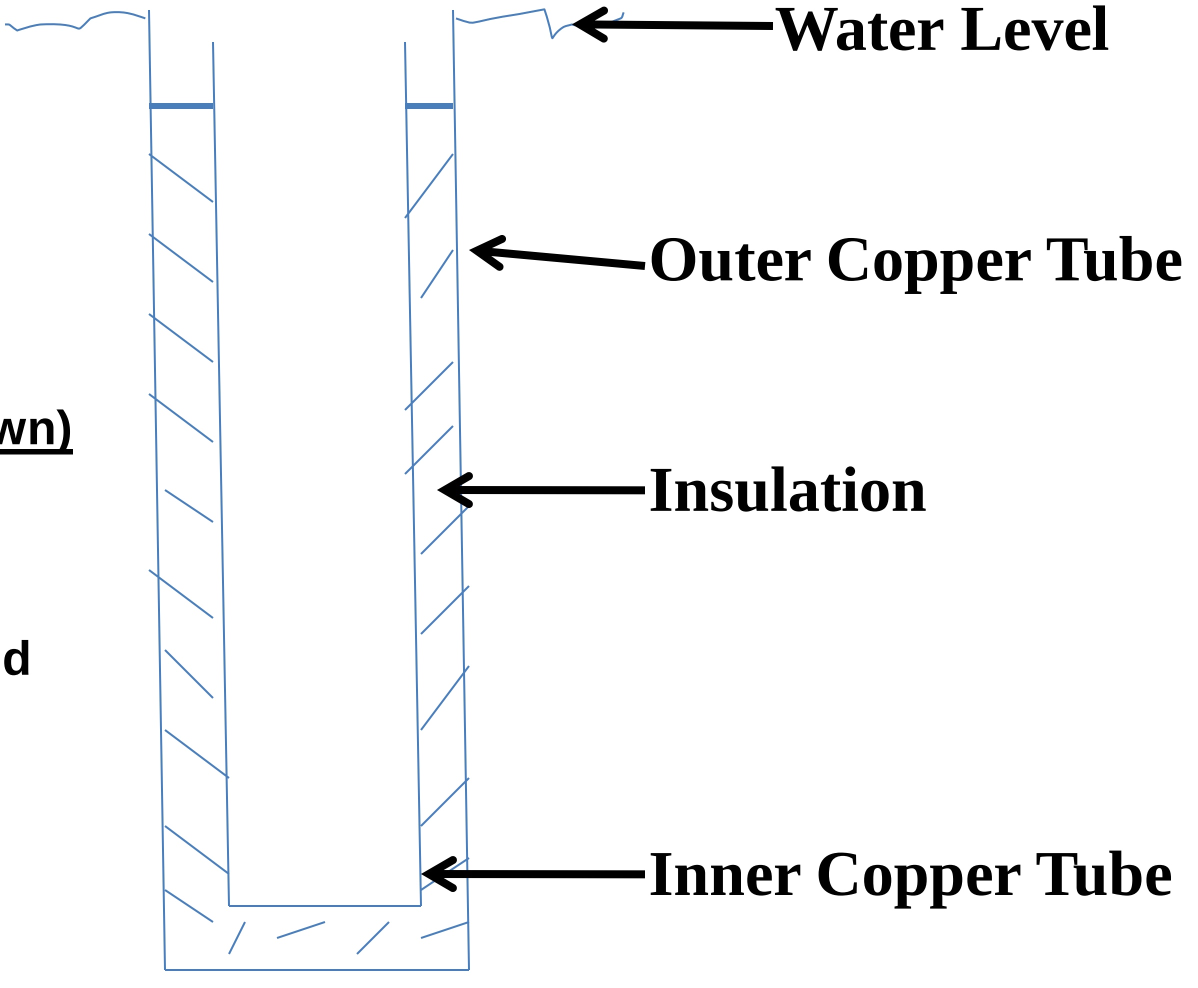
Diagram of New Calorimeter

<u>Outer Copper Tube</u>
5.1 cm x 28 cm

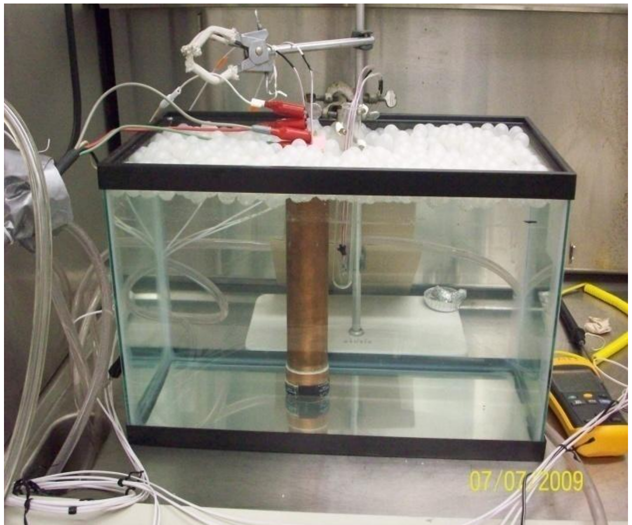
<u>Inner Copper Tube</u>
3.2 cm x 20 cm

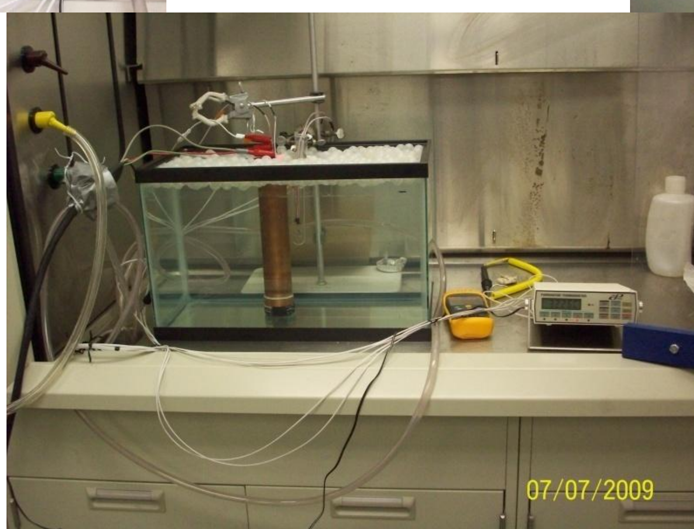
<u>Glass Cell (Not Shown)</u>
2.5 cm x 20 cm

<u>Mobil 1 (5W – 30)</u>
Heat Transfer Fluid
(Not Shown)



Photos of New Calorimeter





Calorimetric Equations (Heat Transfer by Conduction)

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

Assuming $P_H + P_X + P_R = 0$ in control experiments

$$P_{calor} = P_{EI} + P_C + P_{gas} + P_W$$

$$P_{calor} = (E - E_H) I - k_C (T - T_b) + P_{gas} + P_W$$

$$k_C = [(E - E_H) I + P_{gas} + P_W - P_{calor}] / (T - T_b)$$

For $(E - E_H) I >> (P_{gas} + P_W - P_{calor})$

$$k_C = (E - E_H) I / (T - T_b)$$

Note

$P_{calor} = C_p M dT / dt$ (Differential Equation)

Integration of Cooling Curve Equation For Heat Transfer by Conduction

$$C_pMdT / dt = - k_C (T - T_b) + 0 \qquad (I = 0)$$

$$dT / (T - T_b) = (- k_C / C_pM) dt$$

Integrated Equation

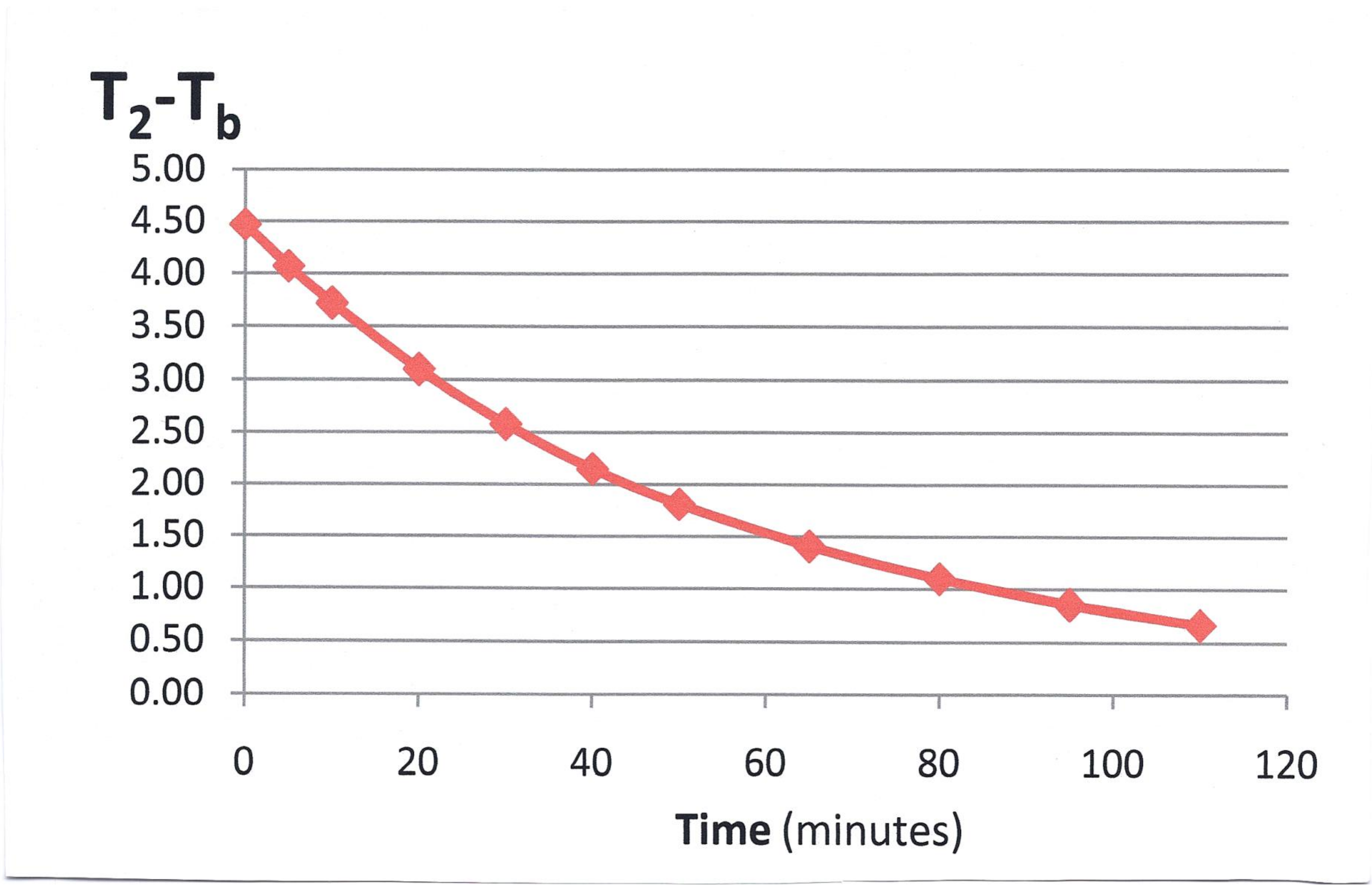
$$\int_{T_o}^{T} dT / (T - T_b) = (- k_C / C_pM) \int_{o}^{t} dt$$

$$\ln (T - T_b) / (T_o - T_b) = (- k_C / C_pM) t$$

Form $y = mx$

m = Slope = $- k_C / C_pM$

Experimental Cooling Curve For New Calorimeter
(Heat Transfer by Conduction)



HEAT CAPACITY FROM COOLING CURVE (Differential Equation)

$$C_pMdT/dt = -k_C(T-T_b)$$

$$C_pM = -k_C(T-T_b) / (dT/dt)$$

For t = 10 minutes (k_C = 0.133 W/k)

dT/dt = -1.08 x10^{-3} K/s

$T - T_b$ = 3.72 K

C_pM = 458 J/K

For t = 30 minutes (k_C = 0.133 W/k)

dT/dt = -8.03 x10^{-4} K/s

$T - T_b$ = 2.58 K

C_pM = 427 J/K

For t = 65 minutes (k_C = 0.133 W/k)

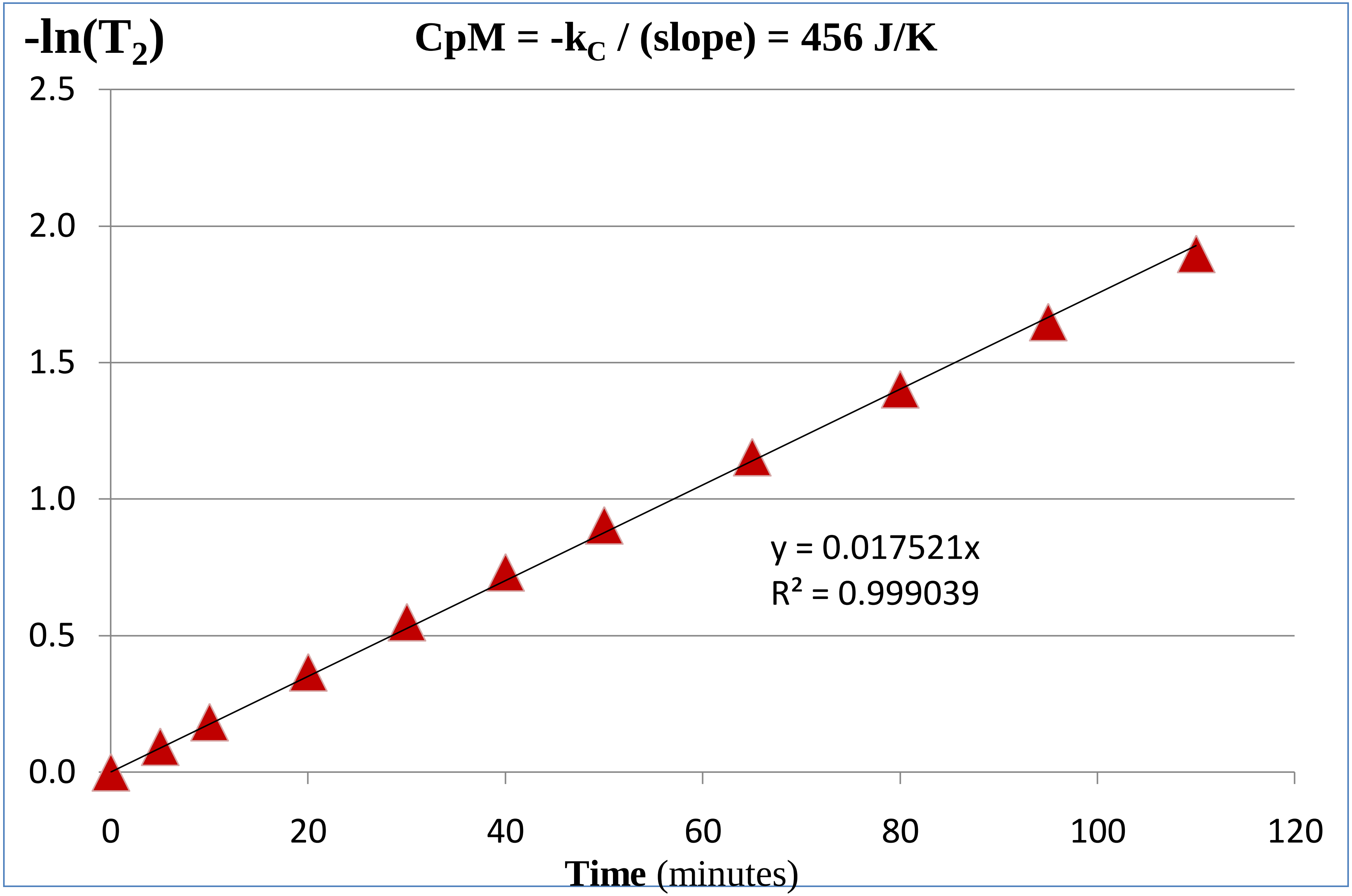
dT/dt = -3.87x10^{-4} K/s

$T - T_b$ = 1.41K

C_pM = 474 J/K

MEAN CpM = 453 ±24 J/K

Cooling Curve Using Integrated Equation
(Heat Transfer By Conduction)



Estimate of Heat Capacity of the Cell, C_pM

50.0 mL H_2O

(50.0 mL)(0.997 g/mL)1mole/18.0g)(72.29 J/mol K)= 200.2 J/K

Copper Tube

(38.6 cm3)(8.92 g/cm^3)(1 mole/63.456g)(24.44 J/mol K) = 132.6 J/K

Mobil -1 Oil

(50.0 mL)(0.80 g/mL)(2.10 J/g k) = 84.0 J/K

Glass Cell

(51.8 g)(0.74 J/g k) = 38.3 J/K

Copper Cathode

(0.160 cm^3)(8.92 g/cm^3)(1 mol/63.456 g)(24.435 J/mol K) = 0.55 J/K

Platinum, Palladium, Nickel

2.0 J/K **TOTAL = 458 J/K**

Integration of Cooling Curve Equation For Heat Transfer by Radiation

$$C_pM dT / dt = - k_R (T^4 - T_b^4) + 0 \qquad (I = 0)$$

$$dT / (T^4 - T_b^4) = (- k_R / C_pM)\, dt$$

Integrated Equation

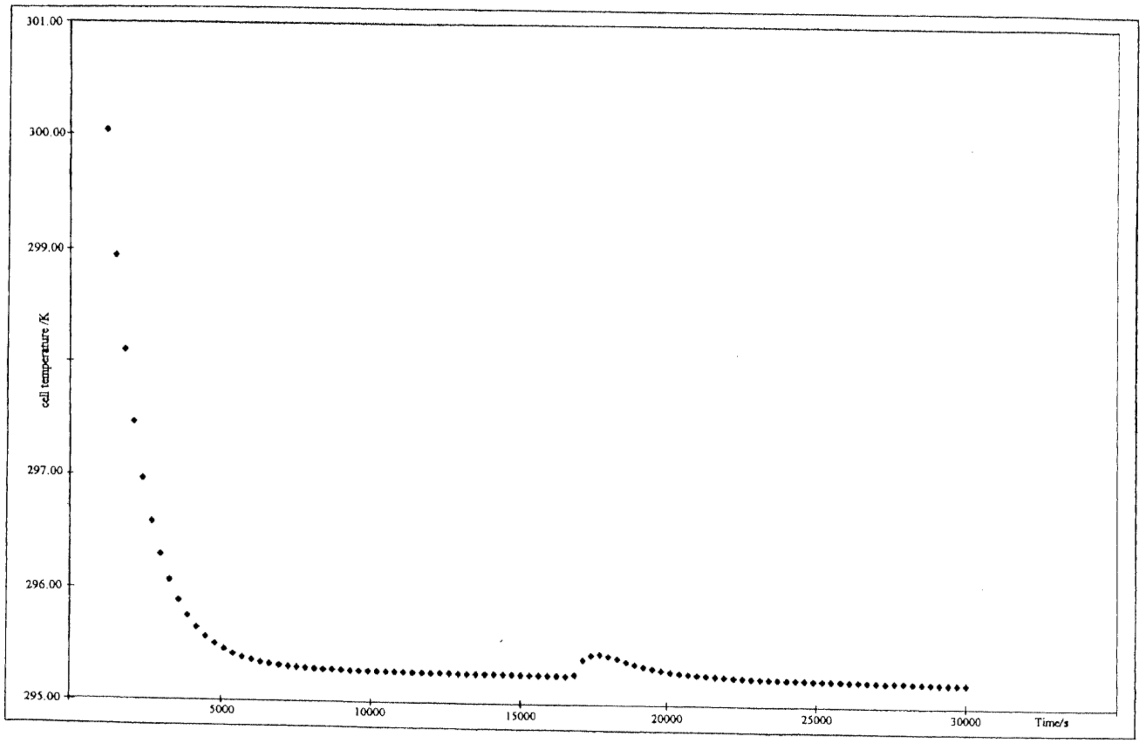
$$\int_{T_o}^{T} dT / (T^4 - T^4_b) = (- k_R / C_pM) \int_{o}^{t} dt$$

$$\ln (T + T_b)(T_o - T_b) / (T_o + T_b)(T - T_b) + 2 \tan^{-1}(T/T_b) - 2 \tan^{-1}(T_o / T_b) = 4T_b^3\, k_R t/C_pM$$

Form $y = mx$

$$m = slope = 4\, T_b^3 k_R / C_pM$$

Cooling Curve For Pd-B in F/P Dewar Calorimeter
(Heat Transfer By Radiation)



Fleischmann's Analysis for Pd-B in the F-P Dewar Calorimeter
(NRL Report, 2001, Fig. A.24)

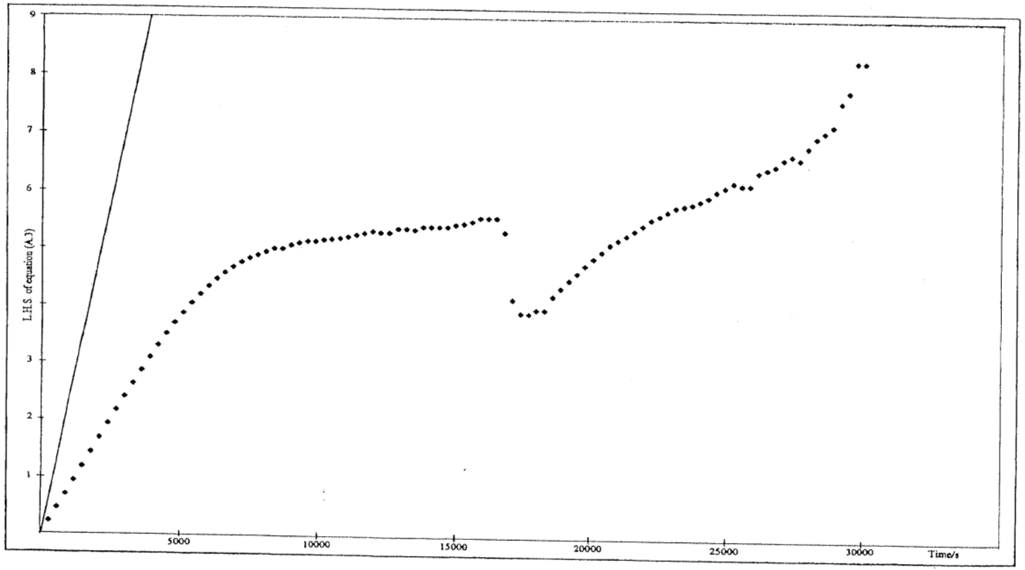


Fig. A.24 The analysis of the initial portion of the "cooling curve" shown in Fig. A.23 according to equation (A.3). The full line shows the R.H.S. of this equation plotted with $C_PM = 28.3\ JK^{-1}$, $(k_R')_{12} = 0.65 \times 10^{-9}\ WK^{-4}$ and $T_{bath} = 295.204$ K.

Stability of Electrolyte Ions During Water Electrolysis

Ion	Possible Anodic Products[a]	Possible Cathodic Products[a]
OH^-	H_2O_2 , O_2	None
$SO_4^{=}$	SO_2 , SO_3 , O_2	$SO_3^{=}$, S , SO_2
NO_3^-	NO[b] , NO_2 , O_2	NO_2^- , N_2 , NH_4^+
Cl^-	Cl_2[c], OCl^- , ClO_2^- , ClO_3^- , ClO_4^-	None
NH_4^+	N_2H_4 , N_2 , NO , NO_3^- , NO_2^- , NO_2 ,, NCl_3[c]	None
Li^+	None	Li[d]
H^+	None	H_2

[a]Effect on pH: Acidic (Red), Neutral (Black), Basic (Blue)

[b]Observed Experimentally by M.H.M ($NO_3^- \rightarrow NO + O_2 + e^-$).

[c]Observed experimentally by M.H.M. in NH_4 Cl solutions.

[d]Requires protective film for stability (SEI).

Results Using Different Electrolytes

0.154 M KNO_3 /Pt (Miles	
27,620 Coulombs	**99.997% H_2O Electrolysis**
Final pH = 10.24	**0.003% NO_3^- Reaction**
Assume $NO^-_3 \rightarrow NO + O_2 + e^-$	**$\Delta E_H = 4.4 \times 10^{-5}$ V**
0.155 M NH4Cl /Pt (Miles)	
50,210 Coulombs	**99.808% H_2O Electrolysis**
Final pH=1.70	**0.192% NH_4^+ Reaction**
Assume 2 $NH^+_4 \rightarrow N_2H_4 + 4\ H^+ + 2e^-$	**$\Delta E_H = 2.8 \times 10^{-3}$ V**
Chlorine and NCl_3 Production	
0.100 M LiOD /Pt(Fleischmann)	
242,000 Coulombs	**99.640% D_2O Electrolysis**
No pH Change (Recombination)	**0.360% O_2 Reduction**
P_X = 1.1±0.1 mW (I = 200 mA)	**$\Delta E_H = 5.50 \times 10^{-3}$ V**

FORMATION AND PROPERTIES OF NITROGEN TRICHLORIDE

FORMATION

Chemical Reaction of NH_4Cl and Cl_2 (pH<4.5)

$$NH_4Cl + 3\,Cl_2 \rightarrow NCl_3 + HCl$$

Electrolysis of NH_4Cl in Acidic Solutions

$$NH_4Cl + 2\,HCl \rightarrow NCl_3 + 3\,H_2$$

PROPERTIES

- ❑ **Yellow Oily Liquid**
- ❑ **Explosive in Pure Form**
- ❑ **Relatively Insoluble In Water**
- ❑ **High Density (1.653 g/cm^3)**
- ❑ **Physical Properties Similar to Carbon Tetrachloride (CCl_4)**

Usually Gone After Third Day

CHEMICAL RECOMBINATION OF NITROGEN TRICHLORIDE
(Reaction with Hydrogen)

$$NCl_3 + 3\,H_2 \rightarrow NH_4Cl + 2\,HCl$$

$$\Delta H° = -\,864\ \text{kJ / mol}$$

- ❖**Slight Solubility in Water**
- ❖**Dissolved NCl_3 Likely Reacts with Hydrogen**
- ❖**Hydrogen Generated At Cathode**
- ❖**Yields Recombination Excess Power**
- ❖**Effect Gone After Third Day**

Fleischmann's Approximate Excess Power Equation (Lower Bound k_c')

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

Assume $P_X = 0$

$$P_{calor} = P_{EI} + 0 + P_H + P_C' + P_{gas} + P_W \quad (2)$$

Equation (1) – Equation (2)

$$0 = P_X + P_C - P_C' = P_X - P_C \Delta T + P_C' \Delta T$$

$$P_X = k_C \Delta T - k_C' \Delta T$$

$$P_X = (k_C - k_C') \Delta T$$

First Results Using Calorimetric Cell B

Date	Solution	I (mA)	(k_C')(W/K)	P_X(mW)[a]
6-23-09	KNO_3[b]	-100	0.132	3
6-24-09	KNO_3[b]	-150	0.133	0
6-25-09	KNO_3[b]	-80	0.127	11
7-1-09	$NH_4Cl+PdCl_2+$ NH_4OH[c]	-50	0.0480	71
7-2-09	$NH_4Cl+PdCl_2+$ NH_4OH[c]	-100	0.119	23
7-7-09	$NH_4Cl+PdCl_2+$ NH_4OH[c]	-200	0.135	-14
7-8-09	$NH_4Cl+PdCl_2+$ NH_4OH[c]	-150	0.130	17[d]
7-9-09	$NH_4Cl+PdCl_2+$ NH_4OH[c]	-100	0.123	30[d]

[a]Based on $P_X=(k_C - k_C')\,\Delta T$ where k_C=0.133 W/k and using experimental ΔT.
[b]0.154 M KNO_3 with platinum cathode
[c]Co-Deposition: 0.151 M NH_4Cl + 0.0143 M $PdCl_2$ + 0.150 M NH_4OH with copper cathode
[d]Solution never recovered from acidic conditions. Final pH = 2.19

CALORIMETRIC DATA SUMMARY FOR 9/11/09 CONTROL (I = 400 mA, Cell B)

Time	$-E_{cell}$ (V)	P_{EI}(W)	ΔT_2(K)	K_2 (W/K)
2:29	5.122	1.4564	11.000	0.1324
2:44	5.121	1.4560	10.995	0.1324
4:01	5.110	1.4516	10.970	0.1323
4:53	5.103	1.4488	10.935	0.1325
5:51	5.094	1.4452	10.915	0.1324
6:46	5.088	1.4428	10.900	0.1324
7:19	5.083	1.4408	10.890	0.1323

$\langle k_2 \rangle = 0.1324 \pm 0.000069$ ($\pm$ 0.052%)

Stable Cell Constant Independent of Electrolyte Level

$\langle Pcalor \rangle$ = (450 J/k) (-0.11 K/17550 s) = -0.0028 W

$\langle k_2 \rangle$ = 0.1327 W/K

SUMMARY

- **New Calorimeter Provides Very Stable Temperature Readings**
- **Stable Cell Constants Independent of Electrolyte Level**
- **Cell Constants In Correct Range**
- **Cooling Curves Provides Heat Capacity (C_pM)**
- **Cooling Curves Sensitive To "Heat After Death"**
- **LiOD and KNO_3 Are Stable Electrolytes**
- **Co-Deposition Control Gives Excess Power Effects When HCl, Cl_2, and NCl_3 are Formed**
- **KNO_3/Pt Provides Stable Control System**
- **NH_4Cl/Pt System Yields HCl, Cl_2, and NCl_3**
- **Most Accurate Calorimetric Results Require Integration of Data**
- **Calorimetry of Deuterium/Palladium Systems In progress**

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