NEW APPROACHES TO ISOPERIBOLIC CALORIMETRY

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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 $k_R = 0.83 \times 10^{-9}$ 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

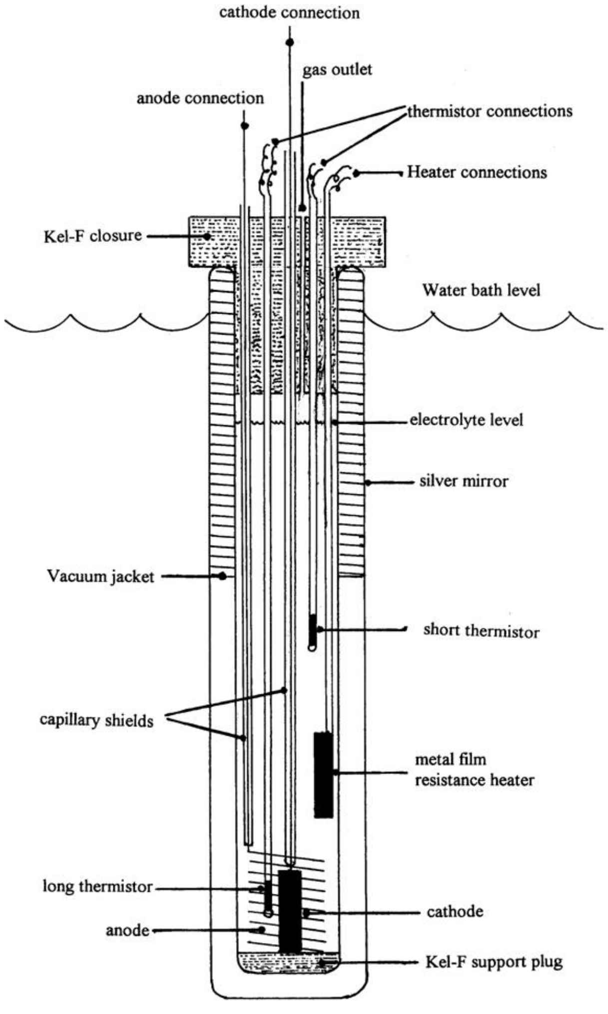


Diagram of the Fleischmann-Pons ICARUS-14 Calorimeter
(Never Constructed)

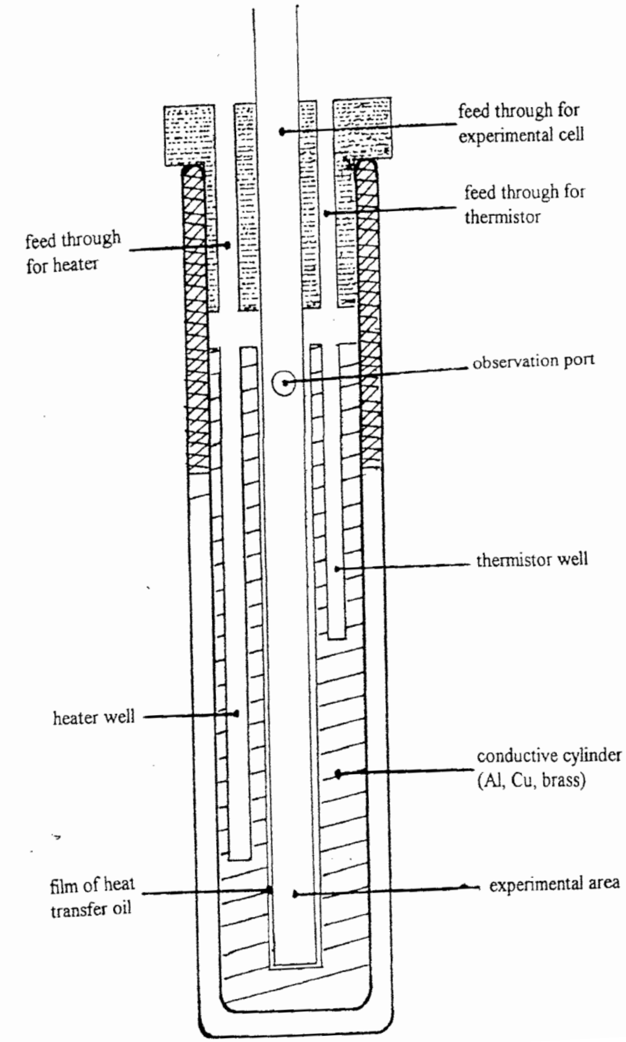


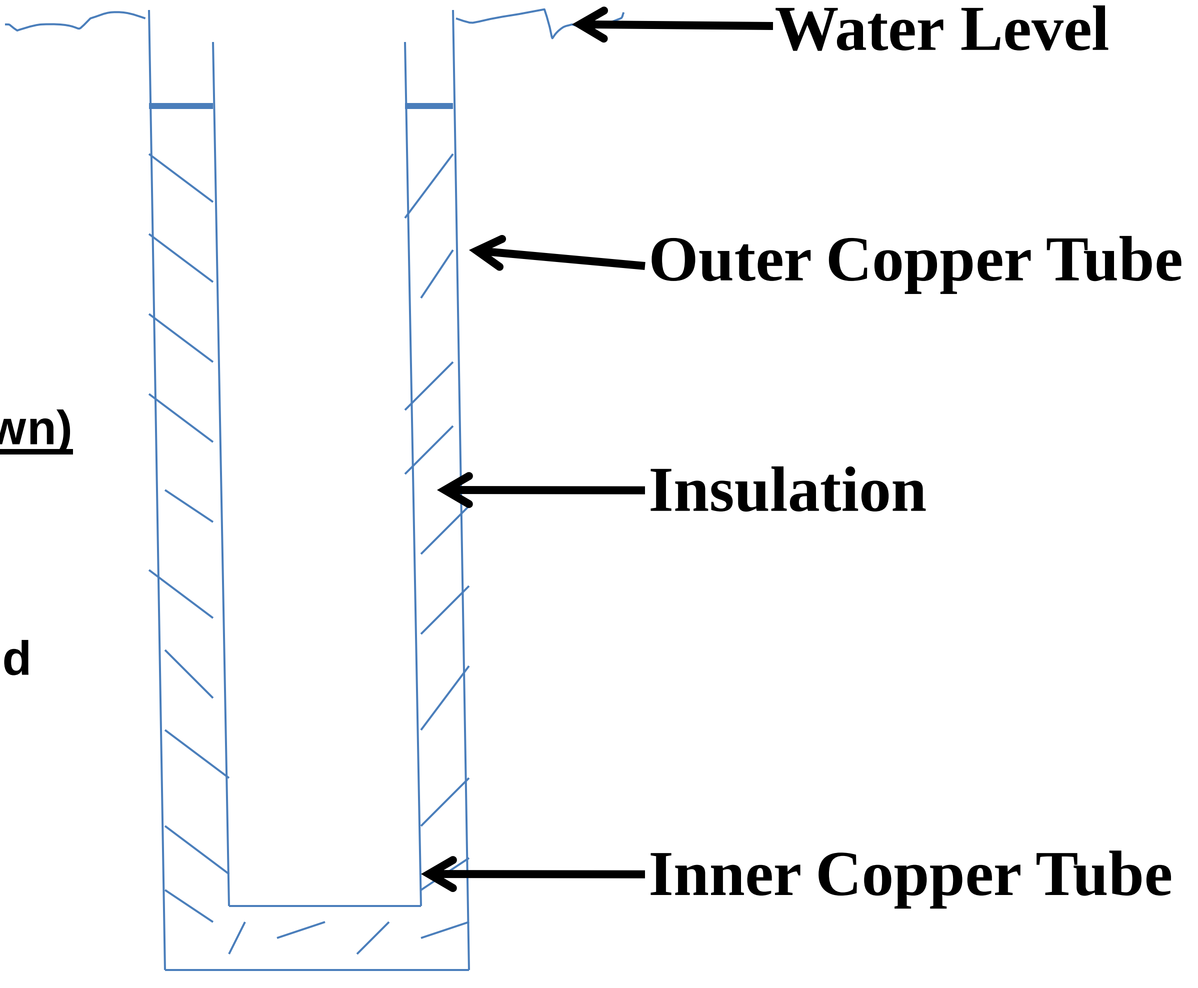
Diagram of New Calorimeter

Outer Copper Tube
5.1 cm x 28 cm

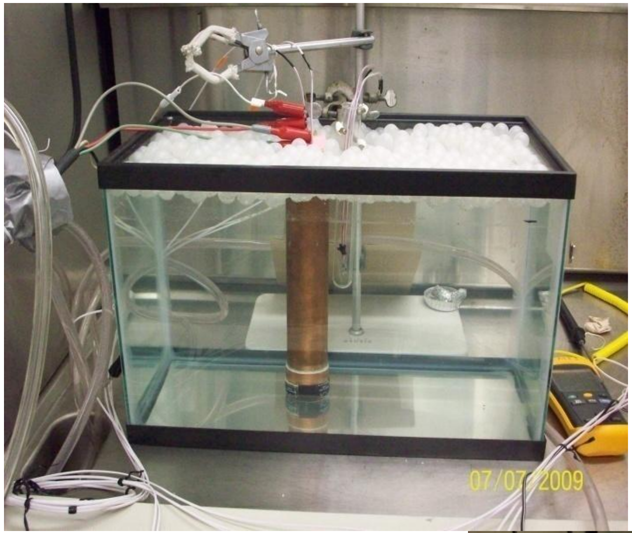
Inner Copper Tube
3.2 cm x 20 cm

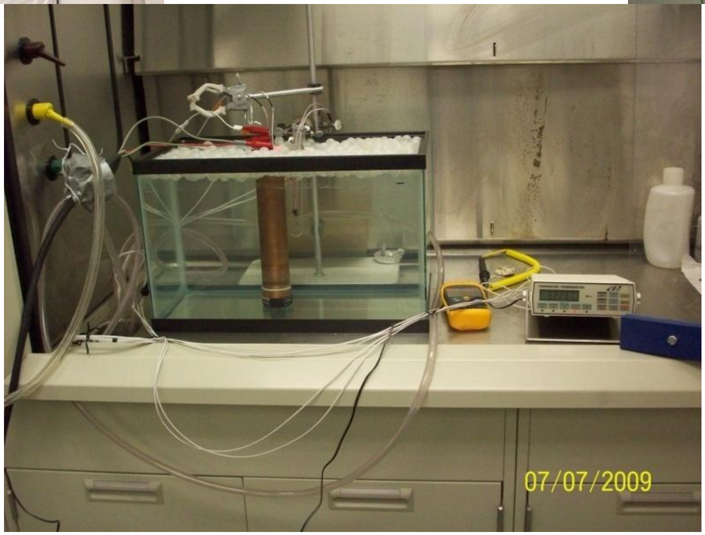
Glass Cell (Not Shown)
2.5 cm x 20 cm

Mobil 1 (5W – 30)
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

$$C_p M dT / dt = - k_C (T - T_b) + 0 \qquad (I = 0)$$

$$dT / (T - T_b) = (- k_C / C_p M) dt$$

Integrated Equation

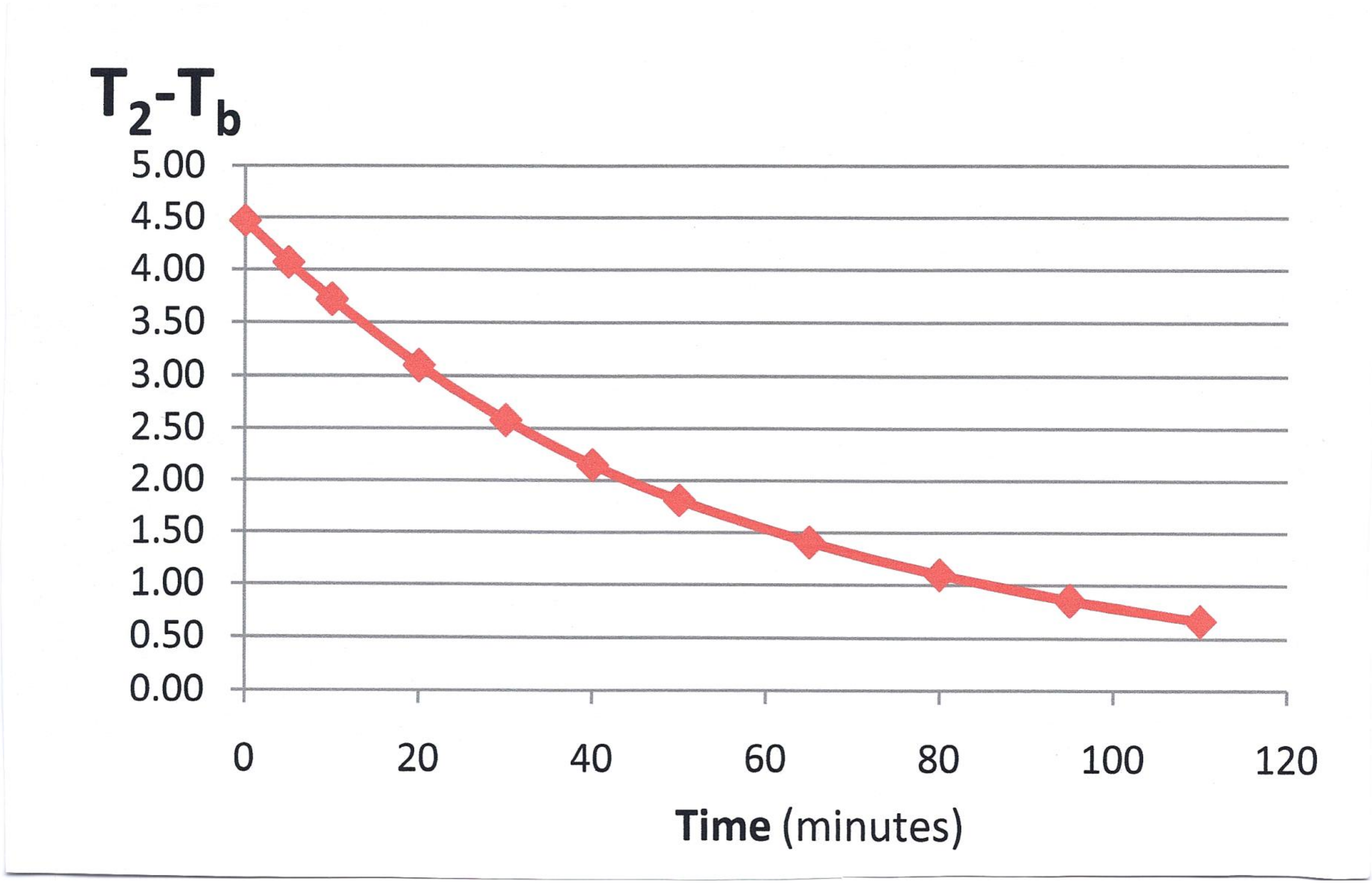
$$\int_{T_o}^{T} dT / (T - T_b) = (- k_C / C_p M) \int_{o}^{t} dt$$

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

Form $y = mx$

m = Slope = $- k_C / C_p M$

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)

$dT/dt = -1.08 \times 10^{-3}$ K/s

$T - T_b = 3.72$ K

$C_pM = 458$ J/K

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

$dT/dt = -8.03 \times 10^{-4}$ K/s

$T - T_b = 2.58$ K

$C_pM = 427$ J/K

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

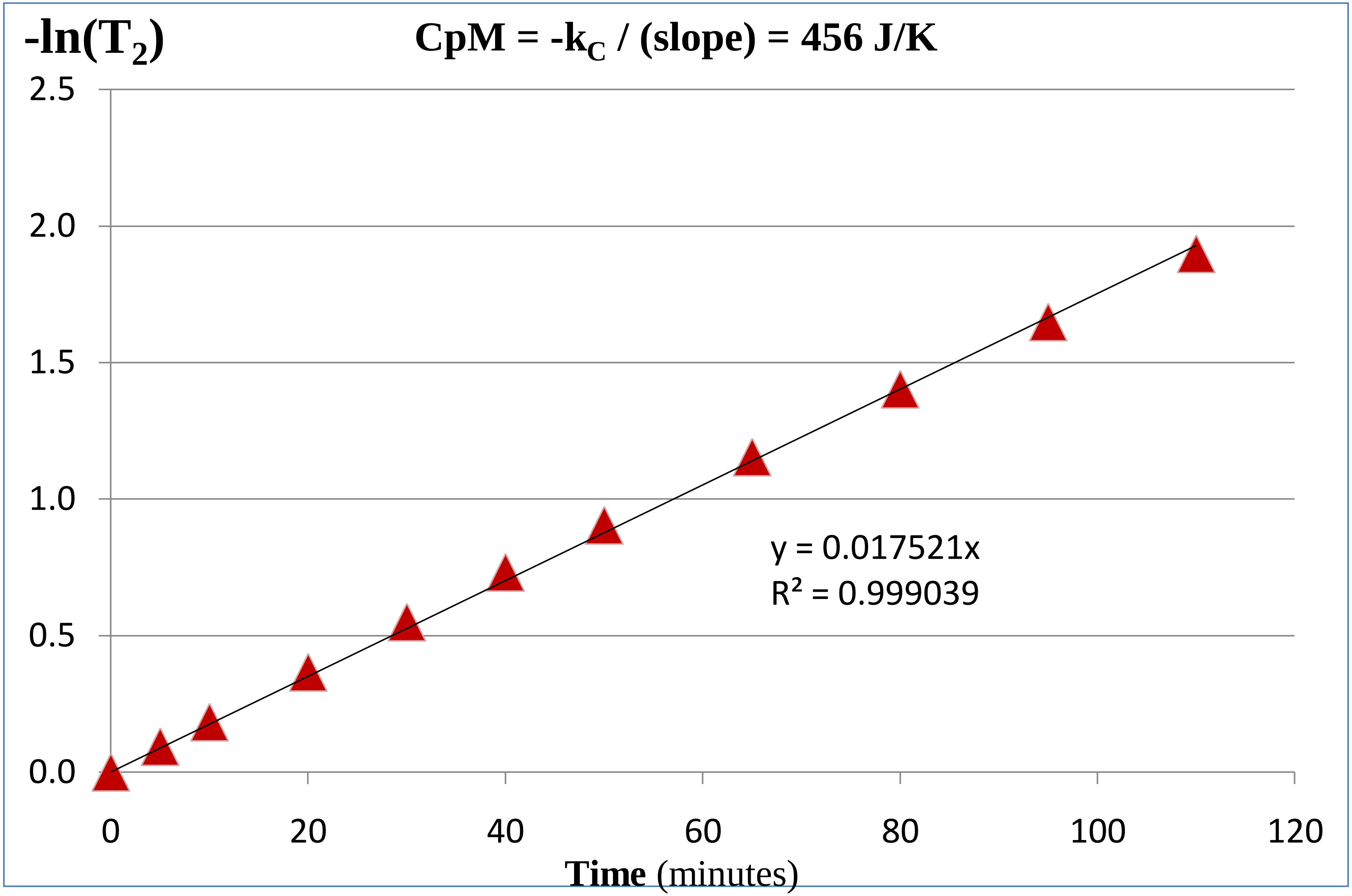
$dT/dt = -3.87 \times 10^{-4}$ K/s

$T - T_b = 1.41$K

$C_pM = 474$ 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

<u>50.0 mL H_2O</u>

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

<u>Copper Tube</u>

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

<u>Mobil -1 Oil</u>

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

<u>Glass Cell</u>

(51.8 g)(0.74 J/g k) = <u>38.3 J/K</u>

<u>Copper Cathode</u>

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

<u>Platinum, Palladium, Nickel</u>

<u>2.0 J/K</u>

TOTAL = 458 J/K

Integration of Cooling Curve Equation For Heat Transfer by Radiation

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

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

Integrated Equation

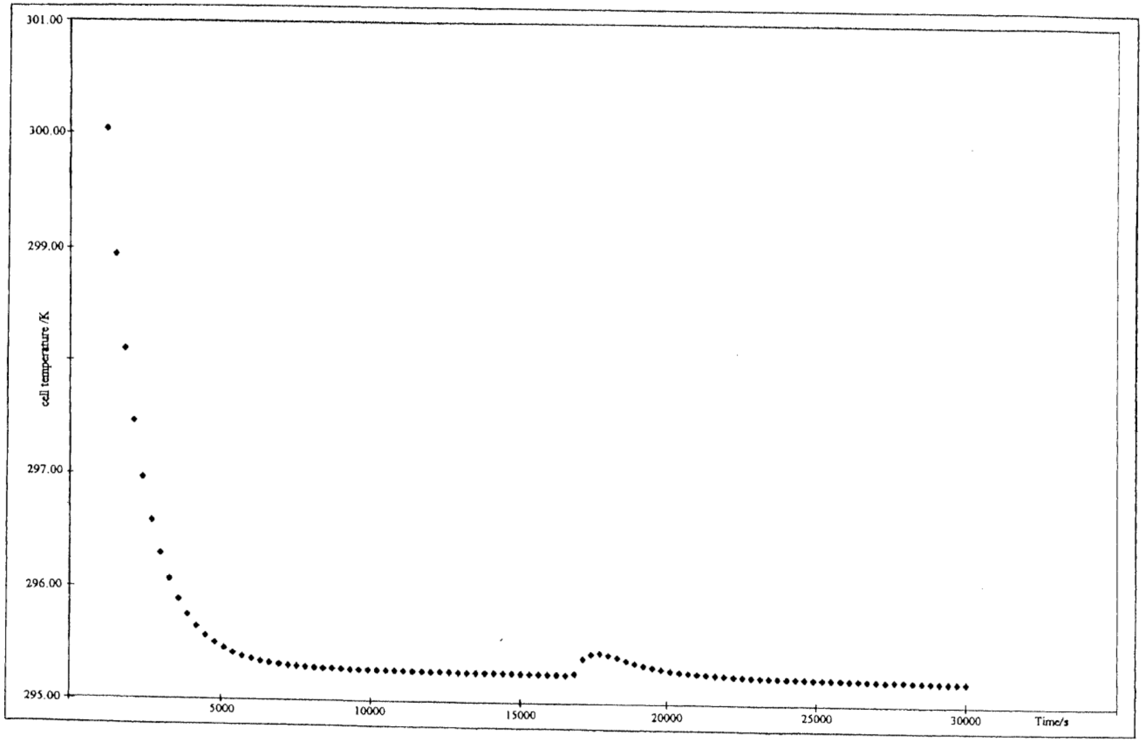
$$\int_{T_o}^{T} dT / (T^4 - T^4_b) = (- k_R / C_p M) \int_{o}^{t} dt$$

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

Form $y = mx$

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

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)

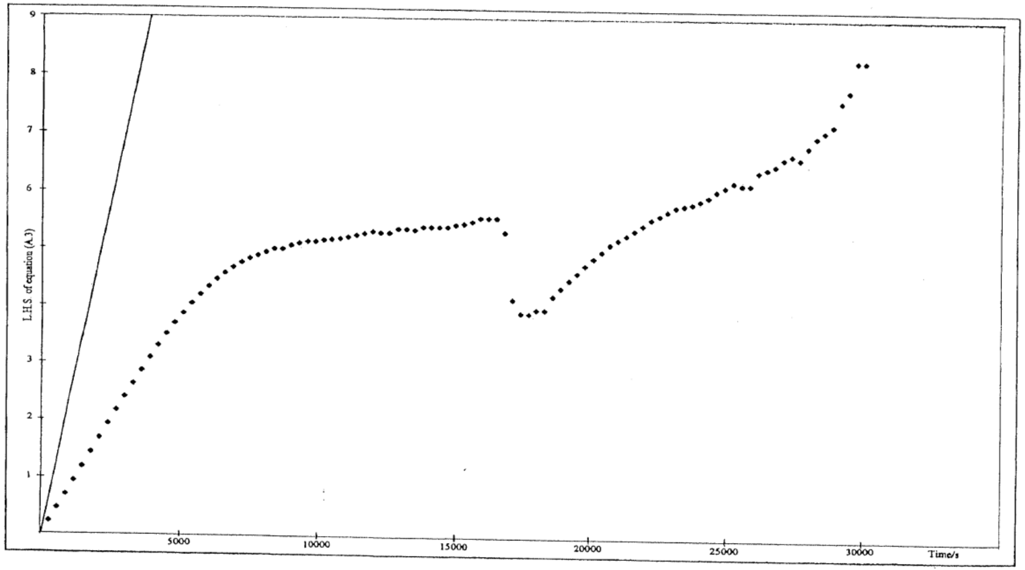


Fig. A.24 The analysis of the initial portion of the "cooling curve" shown in Fig. A.23 according to equation (A.3). The full line shows the R.H.S. of this equation plotted with $C_PM = 28.3\ JK^{-1}$, $(k_R')_{12} = 0.65 \times 10^{-9}\ WK^{-4}$ and $T_{bath} = 295.204$ K.

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

<u>0.154 M KNO_3 /Pt (Miles</u>

27,620 Coulombs

Final pH = 10.24

Assume $NO^-_3 \rightarrow NO + O_2 + e^-$

99.997% H_2O Electrolysis

0.003% NO_3^- Reaction

$\Delta E_H = 4.4 \times 10^{-5}$ V

<u>0.155 M NH4Cl /Pt (Miles)</u>

50,210 Coulombs

Final pH=1.70

Assume $2\ NH^+_4 \rightarrow N_2H_4 + 4\ H^+ + 2e^-$

Chlorine and NCl_3 Production

99.808% H_2O Electrolysis

0.192% NH_4^+ Reaction

$\Delta E_H = 2.8 \times 10^{-3}$ V

<u>0.100 M LiOD /Pt(Fleischmann)</u>

242,000 Coulombs

No pH Change (Recombination)

$P_X = 1.1 \pm 0.1$ mW (I = 200 mA)

99.640% D_2O Electrolysis

0.360% O_2 Reduction

$\Delta E_H = 5.50 \times 10^{-3}$ 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)

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

$$\Delta H° = -\ 864\ kJ\ /\ mol$$

- ❖**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

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

Stable Cell Constant Independent of Electrolyte Level

<Pcalor> = (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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