New approaches to isoperibolic calorimetry

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Abstract. Relatively 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 during electrolysis. Four prototypes were constructed from copper tubing and used different insulating materials. Preliminary tests on two of these new calorimeters show excellent stability for the cell temperature measurements, stable heat transfer coefficients during electrolysis, and precise power measurements.

1. Introduction: design considerations for isoperibolic calorimeters

An important goal for isoperibolic calorimeters is a constant heat transfer coefficient that does not change as the electrolyte level decrease due to the electrolysis and evaporation. All measurements could then be evaluated with a single, predetermined value for the heat transfer coefficient. The placement of the thermistors in a secondary compartment outside the cell has been shown to minimize the cell electrolyte level effect [1-4]. This type of calorimeter can then be modeled as a fluid in which the electrochemical cell serves as a heating element for the substance in the adjacent compartment.

The size of the calorimetric system must be carefully considered in the design. Large systems give slower electrolyte level changes along with larger heat capacities and time constants. Small calorimetric cells yield faster electrolyte level changes and smaller heat capacities and time constants, but their small cell volumes require more frequent makeup of H_2O or D_2O additions. The heat transfer coefficient will also increase with the surface area of the calorimetric system. Adequate stirring of the cell contents by the electrolysis gases requires thin, tall cells where the cell diameter does not exceed 3 or 4 cm. All these factors were carefully considered in selecting design features for these new isoperibolic calorimeters.

2. Experimental details of the calorimetric design

Four prototype isoperibolic calorimeters (A, B, C, D) have been constructed from commercial copper tubing and copper end caps, and two (A, B) have been tested. Each calorimeter consisted of two completely isolated copper cylinders. The outer copper cylinder for each calorimeter had a 5.1 cm (2.0 inch) diameter and a 28 cm height. The inner copper cylinder (3.2 cm x 20 cm) was completely separated from the outer cylinder by the insulating material consisting of either pipe foam insulation (Cell A) or of tightly packed Oregon timber sawdust (Cell B). The glass electrochemical cell (2.5 cm x 20 cm) was a large commercial glass test tube (Kimax). This test tube cell was positioned inside the inner copper cylinder and filled 2/3 full using 50.0 mL of the selected electrolyte. Two thermistors were positioned on opposite sides of the outer wall of the glass tube with each thermistor level with the center of the cathode used. Thermal contact between the glass cell and the inner copper tube was provided by Mobil-1 (5W-30W) synthetic motor oil (50 mL) as the heat conducting fluid. This Mobil-1 oil has a reported density of 0.80 g/mL at 15°C and a heat capacity of 2.10 J/g.K at 80°C. This 50 mL of Mobil-1 oil filled the secondary chamber well above the cell electrolyte level. It is expected that this calorimetric design will provide for high cell operating temperatures up to the boiling point of the selected electrolyte solution. Photographs of the calorimetric cell and experimental arrangements are available electronically (http://iccf15.frascati.enea.it/ICCF15-PRESENTATIONS/S1_O9_Miles.pdf).

3. Review of equations for isoperibolic calorimetry

The mathematical equations that model isoperibolic calorimetry have been fully presented elsewhere [5-8], thus this will only be a brief review. The fundamental modeling equation is

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

where these individual power terms have all been defined elsewhere [5-8]. Equation 1 represents a differential equation because

$$P_{calor} = C_p M dT/dt \qquad (2)$$

where $C_p M$ is the heat capacity of the total calorimetric system expressed in terms of the heat capacity (C_p) and the equivalent moles (M) of H_2O or D_2O.

It is useful in initial calculations to assume that there is no anomalous excess power, $P_X=0$, thus Eq. 1 becomes

$$P_{calor} = P_{EI} + P_H + 0 + P_C{'} + P_R + P_{gas} + P_W \qquad (3)$$

The simple subtraction of Eq. 3 from Eq. 1 yields

$$0 = P_X + P_C - P_C{'} = P_X - k_C \Delta T + k_C{'} \Delta T \qquad (4)$$

or

$$P_X = (k_C - k_C{'}) \Delta T \qquad (5)$$

where $\Delta T = T - T_b$. Therefore, the difference between the true conductive heat transfer coefficient (k_C) and the pseudo heat transfer coefficient ($k_C{'}$) obtained by assuming $P_X = 0$ provides for a simple calculation of the actual excess power via Eq. 5. All of the power terms in Eq. 1, however, should be considered in the determination of $k_C{'}$.

4. Initial experimental results

The use of this new isoperibolic calorimetric design requires the evaluation of the conductive heat transfer coefficient, k_C, and the heat capacity, $C_p M$, of the calorimetric system. Several experiments using H_2O control electrolytes yielded $k_C = 0.164$ W/K for Cell A and $k_C = 0.133$ W/K for Cell B. These cells differ only by the use of foam insulation in Cell A and packed sawdust insulation in Cell B.

The experimental cooling curve obtained by simply turning off the cell current provides a convenient method for determining the heat capacity, $C_p M$, of the calorimetric system. For a H_2O control experiment at zero current, Eq. 1 becomes

$$C_p M dT/dt = -k_C (T-T_b) \qquad (6)$$

This differential equation can be rearranged to

$$dT/(T-T_b) = -(k_C/C_p M)dt \qquad (7)$$

and then integrated to yield

$$-ln (T-T_b) / (T_0-T_b) = (k_C/C_p M)t \qquad (8)$$

This integrated equation is of the form $y = mx$ where the slope (m) is given by $m=k_C/C_p M$.

The experimental cooling curve for Cell B using a H_2O control is present in Figure 1 where T_2 is the cell temperature measured by thermistor 2. This figure shows the expected exponential decrease of $T_2 - T_b$ with time. Figure 2 shows the same data using the integrated Eq. 8. The slope $m=0.01752$ min^{-1} = 2.920×10^{-4} s^{-1}. Therefore $C_p M = k_C/m = 456$ J/K. The heat capacity of the system can also be calculated using the differential equation (Eq. 6) directly, but this is considerably less accurate because of the estimate of dT/dt. From Eq. 6, $C_p M = -k_C(T-Tb) / dT/dt)$. Table 1 presents the value for $C_p M$ obtained directly from Figure 1 at 10, 30, and 65 minutes. The three values calculated for $C_p M$ range from 427 J/K to 485 J/K with a mean of 457±29 J/K. It is obvious that more
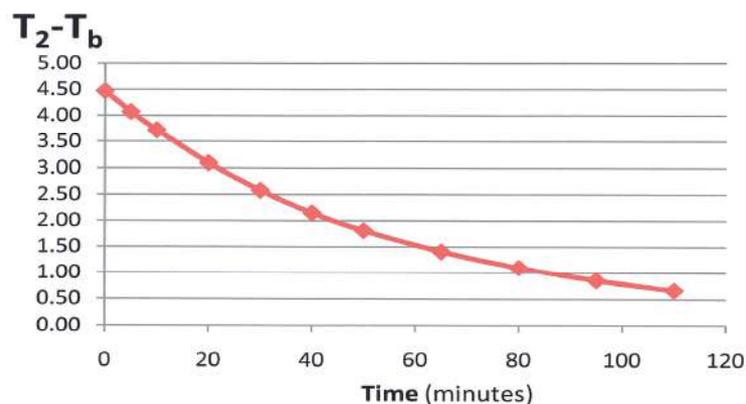
Fig. 1. - Experimental cooling curve for Cell B.

Table 1. Heat capacity (C_pM) for Cell B calculated from the cooling Curve of Fig. 1 using the differential equation (Eq. 8).

T (minutes)	dT_{cell} / dt (K/min)	$T - T_b$(K)	C_pM (J/K)
10	-10.8×10^{-4}	3.72	458
30	-8.03×10^{-4}	2.58	427
65	-3.87×10^{-4}	1.41	485
	Mean C_pM = 457±29 J/K		

accurate results for C_pM are obtained by use of the integrated equation (Eq. 8) where the results can be displayed in a straight line form (Fig. 2). The same is true for all isoperibolic calorimetric results using Eq. 1. Numerical integration of the experimental calorimetric data along with casting them into the straight line form, $y=mx+b$, gives the most accurate results as previously reported [6-9].

The heat capacity of the cell can also be estimated by considering the heat capacity of all materials in the cell or in contact with the cell that undergo the same temperature changes. These calculations give 200 J/K for the 50.0 mL of H_2O used, 133 J/K for the 344 g of the inner copper cylinder, 84 J/K for 50 mL of Mobil-1 oil, 38 J/K for 52 g of the glass cell, and 3 J/K for the copper cathode, platinum wire, palladium and nickel present. The calculated total of 458 J/K is close to the measured value for C_pM.

The time constants for Cells A and B can be readily calculated once k_C and C_pM are known because $\tau = C_pM/k_C$. This yields τ = 3420 s or 57 minutes for Cell B and 46 minutes for Cell A.

It should be noted that cooling curves such as Fig. 1 and 2 provide a useful method for determining lingering excess power effects or "heat-after-death" when electrolysis ceases in active D_2O/Pd experiments. Cell cooling that departs from Eq. 8 or Fig. 2 would be readily apparent. Such studies of cooling curve behavior is planned for future D_2O/Pd experiments. A previous study of Pd-B/D_2O in a Dewar type cell showed marked deviations from the expected cooling curve behavior (see pp. 22-23 and Figs. A.23 and A.24 of Ref. 6).

Although potassium nitrate (KNO_3) has been widely used for years by electrochemists as an inert supporting electrolyte, it has been proposed that shuttle reactions involving nitrates may give false excess power effects [10]. Theoretically, the nitrate ion may be reduced at the cathode to form various gaseous nitrogen oxides, nitrite ions (NO_2^-), or even N_2 or NH_4^+. With the use of special electrocatalyts and conditions, some electrochemical reduction of nitrates is possible [11]. In molten nitrates ($LiNO_3$-KNO_3) at elevated temperatures (250°C), there exists a large 4.5 V electrostability region between the reduction of lithium ions and the oxidation of nitrate ions [12, 13]. This demonstrates the stability of the nitrate ion even at high temperatures. This extreme anodic limit for the nitrate melt is the oxidation of the nitrate ion, $NO_3^- \rightarrow NO + O_2 + e^-$, followed by the further reaction of NO with oxygen to form brown NO_2 gas [12].

Because of the proposed shuttle reactions involving nitrates [10], an initial study using this new isoperibolic calorimeter was the investigation of 0.154 M KNO_3 in Cell B. This study used a platinum wire cathode

(1mm x 15mm) and a platinum coil anode. The H_2O + 0.154 M KNO_3 / Pt system was investigated over several days of electrolysis at currents of 80, 100, and 150 mA. These were no measurable excess power effects. The correct value of $k_C' = 0.133$ W/K was obtained using Cell B and assuming $P_X = 0$. Therefore $k_C - k_C' = 0$ and $P_X = 0$ from Eq. 5. Recent cyclic voltammetric studies on $KNO_3 + NaNO_2$ have confirmed that there are no reversible reactions involving nitrates or nitrites that could act as shuttle reactions.
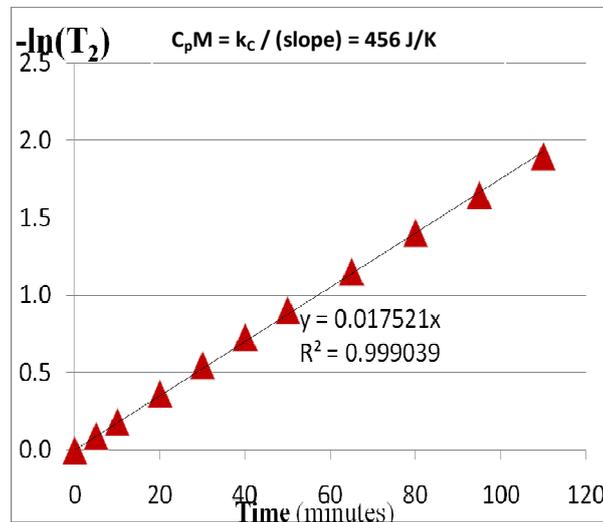

Fig. 2. - Cooling curve data of Fig. 1 using the integrated equation where $-\ln(T_2)$ represents the left-hand side of Eq. 8.

The measured pH of the 0.154 M KNO_3 solution, however, changed from near neutral initially (pH = 7.02) to pH = 10.24 at the end of this study. Any electrochemical reaction of a NO_3^- ion to form a neutral product such as N_2H_2 or N_2 results in the production of OH^- ion to maintain electroneutrality. For the total of 27,626 coulombs used in this study, the observed pH change could be explained by 0.003% of the current being consumed by the reaction of NO_3^-. Therefore, 99.997% of the current was consumed by the expected H_2O electrolysis. The electrochemical reaction of nitrates would, therefore, change the thermoneutral potential (E_H) by only 4.4×10^{-5} V. At the highest current used (150 mA), this nitrate reaction would give a calorimetric error of $(4.4 \times 10^{-5}$ V$)(0.150$A$) = 6.6 \times 10^{-6}$ W or less than 0.007 mW. Therefore, based on this study of 0.154 M KNO_3/Pt, the use of KNO_3 as an inert electrolyte in calorimetric studies would be justified. In a related experiment using 0.158 M $KNO_3 + 0.0577$ M $NaNO_2$, 99.992% of the current (90,720 coulombs) was consumed by H_2O electrolysis. There are no shuttle reactions involving nitrates or nitrites that would give a false excess power effect. In both experiments, the volume of H_2O consumed was larger than the theoretical amount based on Farday's Law.

This new calorimeter was also used to study the 0.15 M NH_4Cl + 0.15 M NH_4OH + 0.025 M $PdCl_2$ co-deposition system in H_2O. Complete results are given elsewhere [14]. In this case, a chemical excess power effect was detected early in the experiment due to the solution becoming acidic (pH=1.25) resulting in chlorine evolution and the formation of nitrogen trichloride (NCl_3). Similar excess power effects were measured by NRL for this same system using a Seebeek calorimeter [15]. With further electrolysis, the solution becomes more basic, chlorine evolution ceases, the NCl_3 dissipates, and normal calorimetric results are observed [14].

In a new study, NH_4Cl + NH_4OH + $PdCl_2$ co-deposition was repeated, but following the palladium co-deposition onto a copper cathode, sufficient LiOH was added to maintain a basic pH. This provided a very stable electrolysis system with no chlorine or NCl_3 formation. The electrolysis of this system using a high current of 400 mA gave evidence for a stable cell constant that was independent of the electrolyte level. The results for this study in Cell B is given in Table 2. The mean cell constant over almost five hours of electrolysis was $\langle k_C \rangle = 0.1324 \pm 0.000069$ W/K. The cell constant never varied by more than ± 0.0001 W/K from the mean value. This is the best evidence to date for an isoperibolic calorimetric cell where the electrolyte level does not affect the cell constant. We were, therefore, successful in attaining our major goal for this new isoperibolic calorimeter.

Table 2. Calorimetric data summary for Cell B with I = 400 mA using the $PdCl_2$ + NH_4Cl + NH_4OH + LiOH electrolyte.

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

$<k_2>$ = 0.1324 ± 0.000069 (± 0.052%)

5. Summary of results

New isoperibolic calorimeters that are relatively inexpensive have been designed, constructed, and tested using several different electrolyte systems. These calorimeters show stable heat transfer coefficients that do not change during electrolysis at high cell currents over long time periods.

Acknowledgements

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