No Steady State For Open Isoperibolic Calorimetry

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A continuing controversy for electrochemical open isoperibolic calorimetry is whether or not a steady state exists for the cell temperature (T) where $dT/dt = 0$. Fleischmann has provided a mathematical solution for the calorimetric differential equation which shows that the cell temperature never reaches a steady state for the F-P Dewar calorimetric cell [1,2]. However, this derivation [1] is complicated and difficult to follow if one does not have Fleischmann's mathematical abilities. A simpler method is to assume that $dT/dt = 0$ and show that the resulting equations cannot be correct under normal electrolysis conditions.

The correct differential equation for open, isoperibolic calorimetry can be expressed by

$$C_p M dT/dt = P_{EI} + P_X + P_H + P_C + P_R + P_G + P_W \qquad [1]$$

where each term is defined elsewhere [3]. If the heat transfer is only by conduction (P_C) then $P_R = 0$. For $dT/dt = 0$, Eq.1 becomes

$$(E - E_H)\, I + P_X + P_H = k_C\,(T - T_b) - P_G - P_W \qquad [2]$$

where $P_{EI} = (E - E_H)\, I$ and $P_C = -k_C\,(T - T_b)$. For the $dT/dt = 0$ conditions, the cell current (I), P_G and P_W would all be constant, and the P_X and P_H terms would be zero or constant. Furthermore, E_H is constant at a given temperature. Therefore, the derivative of all terms in Eq.2 with respect to time (t) yields

$$I\,(dE/dt) = (T - T_b)\, dk_C/dt \qquad [3]$$

This equation states that a steady state cell temperature ($dT/dt = 0$) requires that the rate of change of electrochemical power going into the calorimetric cell must be exactly equal to the rate of change of power going out of the cell by heat conduction. This is a very difficult condition for typical calorimetric cells. The tests of Eq.3 for actual calorimetric experiments yield unrealistic relationships between the experimental values for dE/dt and dk_C/dt. Therefore, the assumption of $dT/dt = 0$ is incorrect. A simple possible solution for Eq.3 is given for $dE/dt = 0$ when either $T - T_b = 0$ or $dk_C/dt = 0$. The $T - T_b = 0$ condition holds only when the cell is off and in thermal equilibrium with the water bath. For $dk_C/dt = 0$, there cannot be any change in the electrolyte level thus both $C_p M$ and k_C would have to be constant. However, both $C_p M$ and k_C change with time due to the electrolysis, hence there is no steady state for the cell temperature [2]. The F-P calorimetric differential equation must always be applied to experimental data for open, isoperibolic calorimeters. Many statements about errors for the F-P calorimetry are due to ignoring this important fact. This is especially true at the beginning for experiments where dT/dt is large and positive [2,3].

The testing of actual experimental data using Eq.3 will be presented. This experimental data shows that Eq.3 completely fails, thus there is no steady state for open isoperibolic calorimetry where $dT/dt=0$.

1. S Pons, Letter with 29 pages of M. Fleischmann Notes, 8 July 1992 (see LENR-CANR, Fleischmann Letters).
2. M.H. Miles, "Excerpts from Martin Fleischmann Letters", J. Condensed Matter Nucl. Sci., Vol. 19, pp. 210-218 (2016).
3. M.H. Miles, "The Fleischmann-Pons Calorimetric Methods, Equations and New Applications", J. Condensed Matter Nucl. Sci., Vol. 24, pp. 1-18 (2017).