THERMAL CONDUCTION AND NON-DIFFERENTIAL TEMPERATURE CORRECTIONS TO THE ENTHALPIC FLOW EQUATION

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ABSTRACT

Conventional calorimetry uses Newton's method, assumes a linear time-invariant system, and determines output power from the temperature rise. Better analyses include thermal transfer by radiation, but most use lumped parameters and ignored terms involving heterogeneity, and those which are not a function of the differential temperature. The multi-ring model of calorimetry has used the corrected thermal mass of the inner ring and the previously neglected thermal mass of the barrier. These are now combined with the effective thermal admittance which superimposes the radiative term with the previously neglected conduction term to derive a better approximation. This method also enables consideration of enthalpic uptake by each barrier in a multi-ring system. This method is important because there is additional data which can be derived by the use of the additional rings, including tardive reconfirmation of the measurement of energy.

INTRODUCTION

Conventional calorimetry examining the enthalpic behavior of electrolysis systems has involved the difficult determination of excess energy from the total heat produced from input electrical energy [1-8]. What is usually done is to use Newton's method and assume a linear time-invariant system. The output power is then determined from the enthalpic flow equation, using the temperature rise, that is $T_1 - T_{bath}$ (defined as θ in several papers). The better calorimetric analyses [2,3] include additional terms involving thermal transfer by radiation such as equation (1).
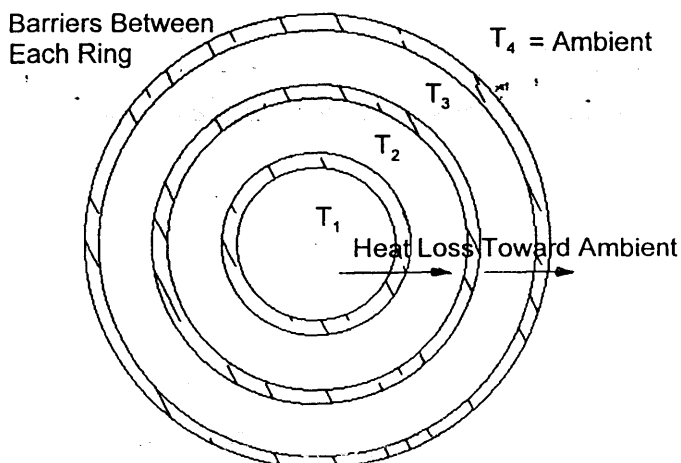
$$C_{P,H_2O,l} M_0 \times \frac{d\Delta\theta}{dt} = [V_{cell}(t) - V_{thermoneutral,bath}] \times I - \frac{3I}{4F} \times \frac{P}{P_{ambient} - P} \times [(C_{P,H_2O,g} - C_{P,H_2O,l}) \times \Delta\theta + L_{H_2O}]$$

$$+ P_x(t) + P_h \times [u_{-1}(t) - u_{-1}(t-\tau)] + k_R \times [(\theta_{bath} + \Delta\theta)^4 - \theta_{bath}^4] \tag{1}$$

As discussed [2,3], the left hand term in this differential equation of thermal transfer (1) is the increase in enthalpy within the calorimeter. The terms on the right hand side are the presumed enthalpy input from the electrolysis, the contribution of enthalpy content leaving with the electrolysis gas stream, the putative excess power (if any), the heater calibration pulse (with the Heaviside functions), and the radiative heat transfer to the water bath. There are some major problems, however, with Eq. (1). First, in the left hand term, the lumped parameter increase in enthalpy within the calorimeter is actually composed of several terms. And most important [3], some of them are not even a function of $\Delta\theta$. Three other problems with the equation include the use of the thermo-neutral potential from the bath rather than the cell, the fact that some would object to this subtraction at all, and the admitted lack of thermal conduction term.

SUCCESSIVE SHELLS ENABLE A MULTI-RING SYSTEM

For clarification here, a series of temperatures in shells (Fig. 1) is considered rather than one differential. Therefore rather than θ, the symbols T_1, T_2, T_i are used. $\Delta\theta$ is not used here simply because it is equal

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Barriers Between
Each Ring

T_4 = Ambient

T_3

T_2

T_1

Heat Loss Toward Ambient

to T_1-T_2 but more importantly because there is additional data which can be derived by the use of the additional rings. Because successive rings are involved and used, additional information [enthalpy to ring 2 (previously "bath")] is not lost. It can be added in for each level. This analysis enables inclusion of those terms in the heat and mass transfer equations which are not a function of the differential temperature ($\Delta\theta$). Some of the materials constitute barriers between rings and hence the energy terms have "additive-terms" [i.e. T_1+T_2] terms as opposed to only differential [T_1-T_2] terms [3].

Multiple Ring Calorimetric System A three (3) ring calorimetric system is shown with three barriers which separate the inner electrolyte (not shown, but having temperature T_1) from the ambient (at temperature T_4). system is shown with three barriers which separate the inner electrolyte (not shown, but having temperature T_1) from the ambient (at temperature T_4).

The mathematical solution to the power and energy equations were derived from a quasi-one dimensional model [3,9] which should not be confused with the Q1D model of isotope loading [10,11]. Account in the calculations was taken of the specific heat and mass of all barriers. Given that there were no sudden changes in thermal

Inhomogeneities in the barriers were not considered. Given that there were no sudden changes in thermal diffusion, and ignoring the inhomogeneities and anisotropies, the barriers 1, 2, 3, 4, and 5 remain spatially fixed, thereby making the mathematical solution amenable to a quasi-one dimensional analysis [3]. The boundary conditions are the first ring (containing the electrochemical cuvette and monitored as T_1), the feedback-controlled midrings (T_3 or T_4), and the zone-controlled room temperature. The heat and mass transfer equations between each set of rings determines the excess heater power (both as an incremental term and amplification rate) and excess energy, if any.

DERIVATION OF CORRECTED ENTHALPIC FLOW EQUATION

There remains confusion as to the definition of input power and excess heat [8]. Although power in electrical and power engineering is defined as V*I, classical electrochemistry considers the thermodynamics by simply assuming the steady state is achieved. Although the standard free energy of water [$\Delta G^0_{298}(H_2O)$ = - 237.18 kJ/mol] yields a theoretical decomposition voltage of water [$V_{thresh} = \dfrac{\Delta G}{2F}$] of 1.23 volts, it is the thermo-neutral potential (V_{therm}) which is subtracted from the cell voltage to derive the electrochemical "input power" where the voltage is V_{cell} - V_{therm}. The thermo-neutral potential is based upon the standard free enthalpy of water $\Delta F^0_{298}(H_2O)$ = - 237.18 $kJ/mole$ and is 1.48 volts (light water, 1.54 heavy water) which is the potential which produces gas without temperature change [2,3,6]. Although most calorimetry in the field is directed towards utilization of the thermo-neutral potential [12] it is simply not respected universally [13]. The major reasons are the lack of thermodynamic equilibrium, the use of this number (V_{cell} - V_{therm}) in a denominator, and the lack of evidence that this is isothermal.

These issues are now corrected, including the addition of thermal conduction and the compartmental correction for the rings which enable consideration of enthalpic uptake by each barrier.

$$[C_{P,H_2O,l} M_0 + \sum_i (C_{P,i} M_i)] \times \frac{dT_1}{dt} + \left(\frac{[C_{12} \times M_{12}]}{2} \right) \times \frac{d[T_1 + T_2]}{dt} = [V_{cell} - V_{thermoneutral}] \times I$$

$$- \frac{3I}{4F} \times \frac{P}{P_{ambient} - P} \times \{[(C_{P,H_2O,R} - C_{P,H_2O,l}) \times (T_1 - T_2)] + L_{H_2O} \} +$$

$$P_x(t) + P_h \times [(u_{-1}(t)) - (u_{-1}(t - \tau))] + k_{R_{12}} \times [T_1^4 - T_2^4] + k_{C_{12}} \times [T_1 - T_2] \qquad (2)$$

The solution of Eq. (2) has been discussed elsewhere [3]. Briefly, α_1 is the second term which is the integrated i terms comprising the thermal capacity of ring 1 (electrolyte, electrodes and leads, thermal sensor and leads, and ohmic control and leads).

$$\alpha_1 = [C_1 \times M_1] + [C_{cathode} \times M_{cathode}] + [C_{anode} \times M_{anode}] + [C_{thermistor} \times M_{therm}] + \left[C_{ohmic_{control}} \times M_{ohmic} \right] \quad (3)$$

γ_{12} is the thermal capacity of each jth portion of the barrier, calculated from the specific heat (C_{12}) and mass (M_{12}) of each subbarrier.

$$\gamma_{12} = C_{12} \times M_{12} \quad (4)$$

The zeroth and first order terms of the source heat allow the definition of an effective thermal admittance [Y_{12}]. This includes radiative and conductive components of the barrier between rings 1 and 2.

$$k_R \times [T_1^4 - T_2^4] + k_C \times [(T_1 - T_2] \cong [(k_C + (4 \times k_R \times [T_2]^3)) \times (T_1 - T_2)] \quad (5)$$

The binomial expansion yields the effective thermal admittance [Y_{12}].

$$Y_{12} = (k_C + (4 \times k_R \times [T_2]^3)) \quad (6)$$

In summary, using the quasi-1-dimensional multi-ring calorimetric analysis [3], the corrected thermal mass of the inner ring and the previously neglected thermal mass of the barrier are now combined with additive terms in the enthalpy flow equation to yield an effective thermal admittance [Y_{12}] between the first two rings (i.e., the sample and the bath in the simplest of systems). Although there are limitations with this method, including failure to include possible phase changes within the material [14, 15], this method yields a more accurate derivation of the information sought as has been demonstrated by thermal waveform reconstruction of control enthalpic inputs [3].

TABLE OF VARIABLES			
α_1 thermal capacity in 1st ring due to electrodes, leads, etc.	joules/(K-mole)	P_h heater power	watts
$C_{P,H2O}$ specific heat water light water	joules/(K-mole)	P_x excess enthalpy = Pexcess	watts
$C_{1,2}$ specific heat of first barrier	joules/(K-mole)	P_{H2O} partial pressure of water	torr
$\Delta F^0(H_2O)$ standard free enthalpy water	joules	$P_{electrolysis}$ ohmic control heat	watts
$\Delta G^0(H_2O)$ standard free energy water	joules	$P_{ambient}$ ambient partial pressure	torr
F the Faraday	96484coul/mole	θ temperature	degrees K
Y_{12} thermal capacity 1st barrier	joules/(K-mole)	T_1 temperature inner ring	degrees K
I electrical current	ampere	T_2 temperature second ring	degrees K
k_C thermal conductive coef.	joules/(cm²secK)	$u_{-1}(t)$ Heaviside function	nondimensional
k_R radiative coef.	joules/(cm²secK⁴)	V_{cell} potential across electrochemical cell	volts
L_{H2O} enthalpy of evaporation	joules/mole	$V_{thermoneutral}$ thermoneutral potential (H_2O)	1.48 volts
M_0 mass of electrolyte in ring 1	grams	Y_{12} combined thermal coefficient (conductive and linearized radiative)	joules/(cm²secK)
M_{12} mass of barrier between rings 1,2	grams		

ACKNOWLEDGMENTS

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