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A simplified approach to the thermal behaviour of electrolytic Dewar cell calorimeters

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A simplified approach, based on the concept of an overall heat loss coefficient, is described for the estimation of time-variant temperature profiles. The computation of the loss coefficient from experimental temperature maxima under programmed power input is also discussed.

Nomenclature

A	active heat transfer area (cm^2)
B_0	parameter in power equation (Equation 7) (W)
B_1	parameter in power equation (Equation 7) ($W s^{-1}$)
b	parameter in power equation (Equation 7) (s^{-1})
c_p	electrolyte specific heat capacity, ($kJ kg^{-1} K^{-1}$)
e	surface emissivity
F	Faraday's constant ($96487 C mol^{-1}$)
I	current (A)
M	molar mass of electrolyte ($g mol^{-1}$)
m_0	initial mass of electrolyte (g)
P	power input (W)
T	electrolyte temperature (K)
T_A	ambient temperature (K)
t	time (s)
x	symbol denoting T or T_0
z	valency
ΔG^0	standard free energy of reaction ($J mol^{-1}$)
ΔH^0	standard heat of reaction ($J mol^{-1}$)
ΔH_R	heat of reaction ($J mol^{-1}$)

Greek symbols

α_1	lumped parameter (Equation 3a) (W)
α_2	overall theoretical heat loss coefficient (Equation 3b) ($W K^{-4}$)
α_2'	overall apparent (experimental) heat loss coefficient ($W K^{-4}$)
β_1	lumped parameter (Equation 3c) ($J L^{-1}$)
β_2	lumped parameter (Equation 3d) ($W K^{-1}$)
ε	relative error in overall heat loss coefficient (%)
σ	Stephan-Boltzmann constant, $5.6697 \times 10^{-8} W m^{-2} K^{-4}$

Subscript

m	related to the temperature maximum

1. Introduction

The calorimetry of single-compartment Dewar cells has recently been the subject of considerable interest in connection with the electrolysis of deuterium oxide in the palladium–deuterium–heavy water system, where various enthalpy-generating and enthalpy-consuming components of the overall thermal balance were investigated meticulously [1–10]. While the question of excess thermal energy via electrochemically induced nuclear fusion in this system remains controversial, these studies of calorimetry associated with D_2O electrolysis indicate clearly the experimental and mathematical encumbrance, [for example 1, Appendix 2, 4] required for a rigorous treatment of primary and secondary thermal effects in Dewar cells. The theoretical estimation of the temperature history in such cells requires intricate and time-consuming estimations [1, *loc.cit*] of numerous process parameters, especially if the time dependence of the effective heat transfer coefficient is also taken into account in the thermal balance equations. Since the ratio of the total enthalpy generated to the Joule enthalpy input can apparently be as high as about thirty [1, Fig. 9A] with respect to reference operating conditions during the 'burst' periods of excess enthalpy, the necessity of carrying out a thoroughly elaborate but cumbersome calculation of thermal properties of the Dewar cell for the sake of demonstrating strong bursts becomes doubtful. Conversely, if such bursts cannot be detected experimentally (as stated in [2] and [3]), discrepancies in temperature predicted by an approximate and a rigorous model may not be important from a practical standpoint.

The purpose of this paper is to describe a simplified thermal analysis of a calorimetric Dewar cell in terms of a single nonlinear thermal balance for the prediction of temperature/time variations in the cell, and to demonstrate that under properly programmed power input conditions, the overall heat loss coefficient can be estimated at relatively high accuracy from the thermal balance. This degree of accuracy may obviate in

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appropriate cases the necessity of estimating (theoretically) thermal sub-processes of secondary magnitude and importance. Alternatively, the simplified approach can serve for a rapid approximate estimation of thermal behaviour, to be followed up by the rigorous approach advocated in the cited literature.

2. Theory

2.1. *An analytical solution in the case of constant thermal power input*

In compliance with the basic Dewar cell structure, where the reaction mixture is separated from a heat-sink bath by the cell wall and a vacuum space offering two thermal resistance in series, the heat transport process from cell to sink is considered to be essentially radiation [1], but with the assumption that the active areas receiving and emitting radiation are of equal size and of the same emissivity. This assumption may be relaxed wherever necessary, by considering more complicated configurations, (for example, Equation 5 in [5]). Due to the gas-evolving nature of the overall electrolytic process

$$2D_2O \longrightarrow 2D_2 + O_2 \qquad (1)$$

the active liquid mass in the cell is decreased in time according to Faraday's law of electrolysis. In consequence, the overall (phenomenological) heat balance for the Dewar cell may be written as

$$\left(m_0 - \frac{IMt}{zF}\right)c_p \frac{dT}{dt} = P - \frac{I\Delta H_R}{zF} - \frac{e\sigma A}{2+e}(T^4 - T_A^4) \qquad (2)$$

with $z = 2$ in the case of Equation 1 (the symbol z is retained for the sake of generality); due to the inherently nonlinear nature of Equation 2, a general analytical solution does not exist. An approximate analytical solution may be obtained in the case of a constant thermal power input (P) and also if (i) the emissivity, e, and the active heat transfer area, A, are considered to be constant (the latter assumption may become untenable at excessively long electrolysis times, unless electrolyte replacement (1) is carried out periodically); (ii) ΔH_R is only a weak function of temperature; and (iii) electrolysis is performed at a constant current. If these assumptions apply, Equation 2 may be rewritten in terms of lumped parameters

$$\alpha_1 \equiv P - \frac{I\Delta H_R}{zF} + \frac{e\sigma A}{2+e}T_A^4 \qquad (3a)$$

$$\alpha_2 \equiv \frac{e\sigma A}{2+e} \qquad (3b)$$

$$\beta_1 \equiv m_0 c_p \qquad (3c)$$

$$\beta_2 \equiv \frac{IMc_p}{zF} \qquad (3d)$$

as

$$\frac{dT}{dt} = \frac{\alpha_1 - \alpha_2 T^4}{\beta_1 - \beta_2 t} \qquad (4)$$

with associated initial condition $t = 0$; $T = T_0$. The solution of Equation 4 via elementary rules of integral calculus may be written in the dimensionless form

$$\phi(T) = \phi(T_0) + \frac{\alpha_2}{\beta_2}\left(\frac{\alpha_1}{\alpha_2}\right)^{3/4} \ln \frac{\beta_1}{\beta_1 - \beta_2(t)} \qquad (5a)$$

where

$$\phi(x) \equiv \tfrac{1}{2}\ln \frac{(\alpha_1/\alpha_2)^{1/4} + x}{(\alpha_1/\alpha_2)^{1/4} - x} + \tan^{-1}(\alpha_2/\alpha_1)^{1/4}x \qquad (5b)$$

x denoting T_0 or T. The $T(t)$ relationship may be obtained by means of ϕ-plots illustrated numerically in the sequel.

2.2. *Solutions in the case of varying thermal power inputs*

The assumption of a constant thermal power may be a reasonable approximation when parasitic power losses are sufficiently low to allow the input electric power input thermal power hypothesis, and when the effective cell resistance varies only slightly (e.g. over a sufficiently short time period). In other instances the term P in Equation 2 becomes time variant and the thermal balance equation requires a numerical solution. Of all temperature profiles the cell can exhibit under varying power input conditions, those having local temperature extremes are of special importance, because the apparent overall heat loss coefficient may be readily estimated from the experimentally observed extremes. Since at an extremum the temperature derivative becomes zero, it follows from Equation 2 that an estimate of the overall heat loss coefficient may be computed as

$$\alpha_2' = \frac{P(t_m) - (I\Delta H_R/zF)}{T_m^4 - T_A^4} \qquad (6)$$

where the symbol α_2' is used to distinguish this quantity from the theoretical quantity of $\alpha_2 = e\sigma A/(2 + e)$. In such an experiment the input power $P(t)$ has to be programmed to result in a smooth temperature maximum or minimum observed at some intermediate temperature t_m. Among many possible choices the function family

$$P(t) = B_0 + B_1 t \exp(-bt) \qquad (7)$$

with adjustable parameters B_0, B_1 and b may be attractive as shown in the next section. It is important to avoid power inputs resulting in a sharp break in the temperature/time profile (even if the break point is an extremum), for the time derivative does not exist at break points; a trivial example is the $|t|$ function which at $t = 0$ has a minimum, but no derivative.

3. Numerical illustration

In Table 1 numerical values of the parameters of a Dewar cell are assembled: resemblance to an earlier cell [1] is incomplete, due to partially available information. The temperature increase, predicted by the analytical solution is compared in Table 2 to the

Table 1. Parameters of a Dewar cell for the numerical illustration of its thermal behaviour (constant power input)

Parameter	*Numerical value and unit*
Initial mass of electrolyte (m_0)	60.745 g
Specific heat capacity of electrolyte (c_p)	4.212 (kJ kg^{-1} K^{-1})
Molar mass (M)	20.0276 (g mol^{-1})
Active heat transfer area (A)	97.817 cm^2
Ambient temperature (T_A)	298.15 K
Initial electrolyte temperature (T_0)	298.15 K
Surface emissivity (e)	0.92
Power input (P)*	3.68; 1.84
Heat of reaction (ΔH_R)	$\sim \Delta H^0 = 294.73$ kJ (mol $D_2O(l)$)$^{-1}$
α_1	3.861 (P = 3.68) W 2.021 (P = 1.84) W
Overall heat loss coefficient (α_2)	1.747 × 10^{-10} W K^{-4}
β_1	255.86 J K^{-1}
β_2	3.54 × 10^{-4} W K^{-1}
$\phi(T_0)$	1.6868 (P = 3.68) 2.2603 (P = 1.84)

* Using Fig. 4c [1] as a guide, a cell voltage drop of 4.6 V was chosen with a current of 800 mA and 400 mA, respectively. Parasitic power losses are neglected.

numerical solution of Equation 4, where a standard Richardson's extrapolation/Romberg quadrature algorithm [11] was used for integration. The graphical procedure shown in Fig. 1 is a convenient means of obtaining the analytical $T(t)$ estimates via Equation 5: ϕ_1 denotes the explicit temperature dependent function given by Equation 5b and ϕ_2 denotes the explicit time dependent function given by Equation 5a, for a specified value of T_0, which sets the numerical value $\phi(T_0)$. The analytical and numerical calculations agree at a less than 1% relative error. The time interval of the simulated process is well below the depletion limit of about 201 h; in the experiments of Fleischmann *et al.* [1] cell electrolyte volumes were replenished at 12–48 h intervals.

The estimation of the apparent overall heat loss coefficient is illustrated in Fig. 2; in order to test the reliability of Equation 6 for the purpose of estimation, the temperature variation was simulated by programming the power input Equation 7 with $B_0 = 2.5$ W, $B_1 = 0.001$ W s^{-1} and $b = 2 \times 10^{-4}$ s^{-1}.

The maximum temperature of 375.77 K is reached at $t_m \simeq 14500$ s, where $P = 3.2978$ W, hence Equation 6 yields the $\alpha_2' = 1.7445 \times 10^{-10}$ W K^{-4} estimate. A computed solution with a finer time-interval grid yields $t_m \simeq 14480$ s and $P = 3.2999$ W, hence $\alpha_2' = 1.7472 \times 10^{-10}$ W K^{-4} is computed (the corresponding time derivatives are -9.5×10^{-6} K s^{-1} and -8.34×10^{-7} K s^{-1} respectively). Comparison with $\alpha_2 = 1.747 \times 10^{-10}$ W K^{-4} indicates that the overall heat loss coefficient can be reliably obtained from carefully monitored *experimental* temperature and input power measurements where α_2 is not *a priori* known. An experimental accuracy of this magnitude is, in fact, not necessary since, as indicated in Table 3, even a one percent relative error in the determination of the overall heat loss coefficient from experimental temperature maxima would induce a very small divergence in the computed temperature profile, and it would not mask the observation of excessive enthalpy generating phenomena (if they do occur) in the Dewar cell.

Table 2. Thermal behaviour of the Dewar cell in the numerical illustration with constant power input (T_0 = 298.15 K)

	Time/s	*Temperature/K*	
		*Eq. 5/Fig. 1**	*Numerical solution of Eq. 4*
(a) P = 3.68 W	1 000	308.5	307.51
	2 000	317.5	316.16
	5 000	336.2	337.93
	10 000	364.0	361.73
(b) P = 1.84 W	1 000	300.0	300.57
	2 000	303.0	302.83
	5 000	307.5	308.65
	10 000	315.0	315.73

* Figure 1 illustrates the P = 3.68 W case; a similar plot, not shown here, has also been used for the P = 1.84 W case.

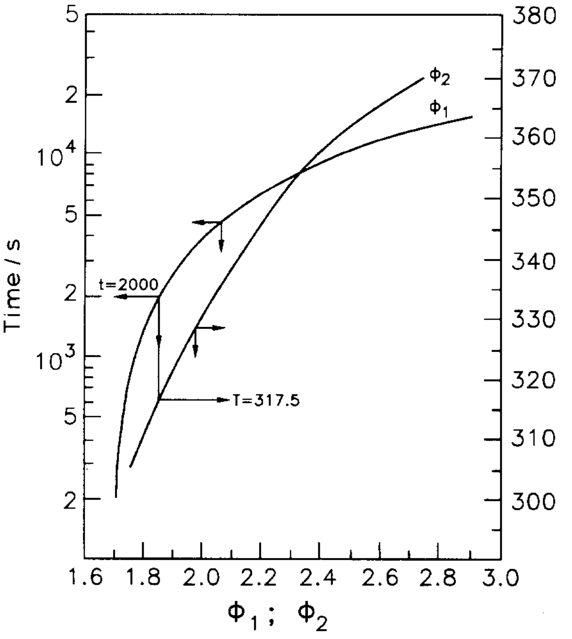

Fig. 1. Graphical aid for the analytical solution of the thermal balance (Equations 4 and 5) in the case of a constant power input.

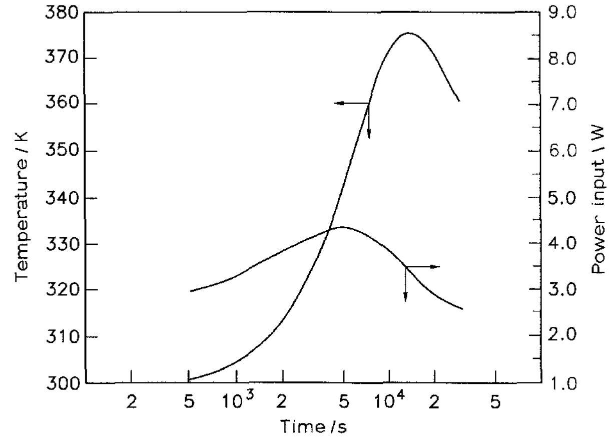

Fig. 2. Thermal behaviour of the Dewar cell with a power input given by Equation 7 with $B_0 = 2.5\,\mathrm{W}$, $B_1 = 0.001\,\mathrm{W\,s^{-1}}$ and $b = 2 \times 10^{-4}\,\mathrm{s^{-1}}$.

4. Final remarks

The foregoing analysis is limited to certain simplifying assumptions (invariance of the active heat transfer area, negligible temperature-dependence of the liquid phase specific heat capacity and the overall heat of reaction in the temperature range of interest), whose removal, if necessary, does not alter the principle of the approach. Similarly, the method can accommodate power inputs of arbitrary time-dependence, which are mathematically more complicated than Equation 7; one can envisage power inputs yielding a temperature minimum *and* a maximum during the same experiment from which two estimates of α_2 can be obtained for the detection of measurement reliability. On the other end of the scale, if in a Dewar cell mass depletion and time variations of power may be neglected, the analysis is simplified to an earlier model [12] requiring a modicum of computation.

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Table 3. Sensitivity analysis of determination errors in the overall heat loss coefficient for the numerical illustration

	Time/s	*Predicted temperature (K) at error level* $\varepsilon \equiv 100\Delta\alpha_2'/\alpha_2'$, %		
		$\varepsilon = -1$	$\varepsilon = 0$	$\varepsilon = +1$
(a) $P = 3.68\,\mathrm{W}$	500	302.94	302.92	302.90
	1 000	307.56	307.51	307.45
	5 000	338.22	337.93	337.64
	10 000	362.29	361.73	361.17
	15 000	375.03	374.29	373.55
(b) $P = 1.84\,\mathrm{W}$	500	299.41	299.38	299.36
	1 000	300.63	300.58	300.52
	5 000	308.90	308.65	308.41
	10 000	316.16	315.73	315.30
	15 000	320.91	320.34	319.78

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