Some comments on the paper Analysis of Experiments on Calorimetry of LiOD/D$_2$O Electrochemical Cells, R.H. Wilson et al., J. Electroanal. Chem., 332 (1992) 1 [*]

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Abstract

We comment here on the title paper and find that it is a series of misconceptions and misrepresentations of previous reports by Fleischmann, Pons and co-workers. It is shown that the conclusions reached by the authors lead to gross errors in the prediction of the observed responses of the electrochemical calorimeters described in the original work and that the correct methods of analyses are indeed those we originally described as well as those which have been outlined in subsequent publications. We find that the authors have not validated their own methods and have not provided sufficient information to allow assessment of their work.

INTRODUCTION

In our major paper on the calorimetry of Pd cathodes polarized in D$_2$O [2] we used two methods of evaluating the excess enthalpy generated in these systems (above that which can be attributed to the enthalpy input) that designated:

"Approximate specific Q_{excess}/W cm^{-3}" (Method 1)

"Specific Q_{excess} from regression analysis/W cm^{-3}" (Method 2).

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[*] Ref. 1.

In two further papers on the subject [3–6] we have used additionally:

"Point by point evaluation of Q_{excess}" (Method 3)

"Kalman filtering" (Method 4)

and Kalman filtering has also been used in an independent evaluation of some of the data which we collected at the National Cold Fusion Institute (NCFI), Salt Lake City [7]; see also ref. 8.

The major claim made in the paper by Wilson et al. [1] is that the calibration of our calorimeters as used in Method 1 was in error and, in particular, that we overestimated the heat transfer coefficients of the cells and therefore also Q_{excess}. In making this claim, the authors have devised a further method of data treatment which we will designate:

"General Electric (GE) approximate method of data analysis" (Method 5)

and for the purposes of this paper, we will also designate a further method which is based on the estimation of a lower bound of k'_R:

"Complete distrust of all methods of calibration" (Method 6).

The authors further report that they have made extensive sets of calorimetric measurements and that these did not give excess enthalpies for any of their experiments.

In the present comment we show that the GE method (Method 5) and our own approximate method (Method 1) are, in fact, equivalent although they estimate the thermal balance at different times along the temperature $(\Delta\vartheta)$–time (t) profile. Both are based on the application of the "steady-state hypothesis" to the differential equations which model the calorimeters. This approach is known to give results of only limited accuracy in other fields of research (although Method 1 would be expected to be somewhat more accurate than Method 5). We show here again (compare refs. 2–10) that accurate estimates of the heat transfer coefficients and of the excess enthalpy (as well as of the other parameters of the models) must be based on the comparison of the integrated forms of the differential equations with the experimental data, and we comment on some other issues raised in the critique [1]; more detailed comments will be given elsewhere [9].

THE DESIGN AND MODELLING OF THE CALORIMETERS

In the experiments which we carried out up to October 1989 (and which formed the basis of our first full-length publication [2]) we used a range of Dewar-type electrochemical cells of various sizes so as to achieve a range of heat transfer rates. We no longer have the full range of these cells to hand but drawings approximately to scale of cells close to the smallest and largest of those made in 1988 are shown in Figs. 1(A) and (B). The cells were designed to allow accurate measurements to be made at enthalpy inputs lying in the range 0.1–4 W. However, because of inadequate evacuation of the "vacuum gap" the heat transfer rates were up to double those predicted from the Stefan Boltzmann coefficient and the radiant surface area, as has also been noted by the group at GE [1], i.e. these rates lay in
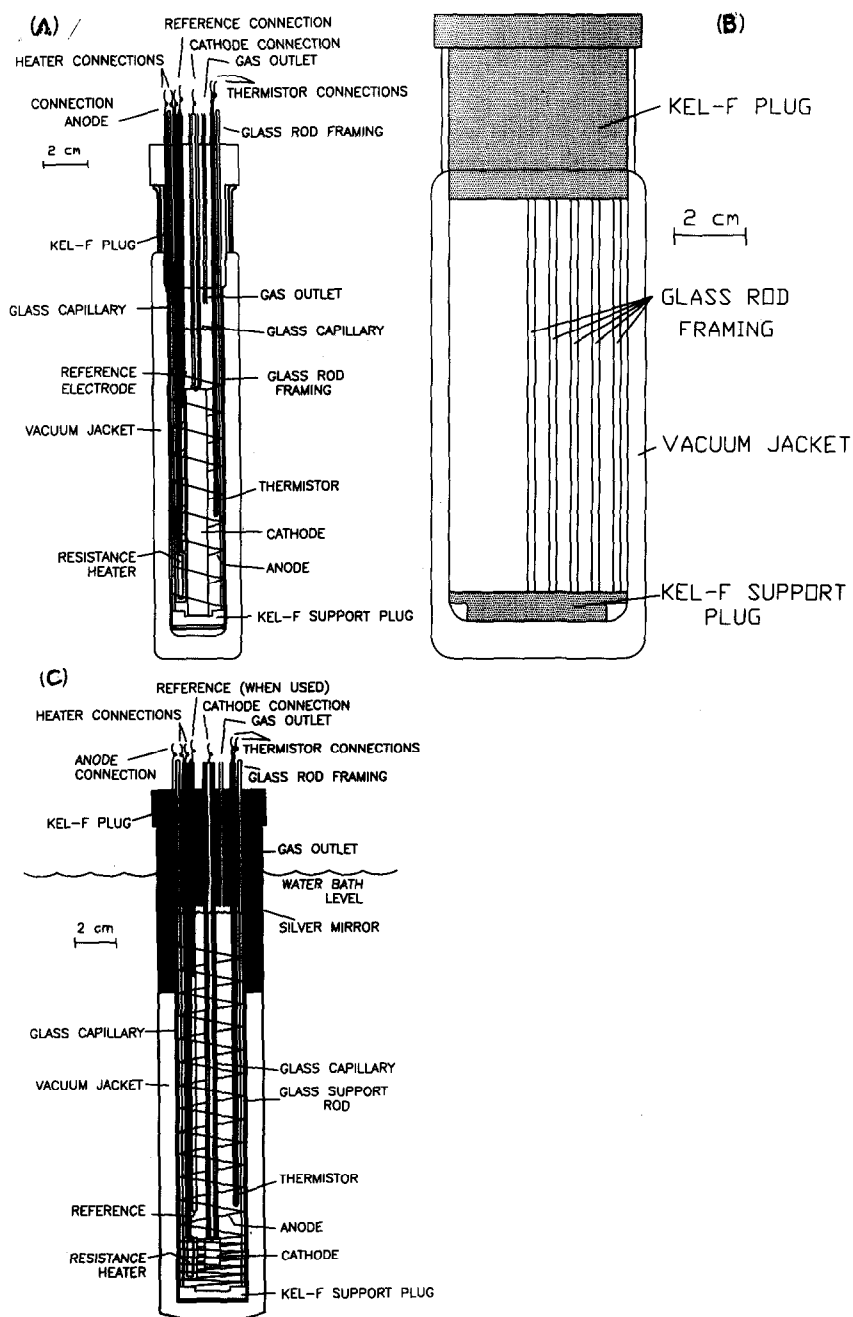
Fig. 1. Single compartment vacuum Dewar calorimeter cells used in 1988 and 1989. (A) small and (B) large calorimeters with mixed conductive and radiative heat transfer; (C) silvered calorimeter characterized by radiative heat transfer.

the range 0.2–8 W. Our specification of "accurate measurements" was that all measured changes in temperature should exceed 2°C when these temperatures were measured to ±0.01°C and that the cell temperatures should not exceed 50°C when that of the surrounding water baths was 30°C. The lowering of the thermostat temperature to 15°C or 5°C allowed us to achieve enthalpy inputs up to 19 W while still restricting the cell temperature to 50°C.

In practice, the projected performance had to be somewhat degraded because the pressure of events at that time (and since then also!) forced us to restrict measurements to the lower end of the size range of our cells. This in turn meant that we had to accept data collected at cell temperatures up to 60°C for parts of the work reported in ref. 2.

In our experiments carried out since October 1989 we have made a simple modification to some of our cells; this is shown in Fig. 1(C). Although this change is simple, it has a marked effect on the modelling: the silvering of the top section of the Dewars ensures that heat transfer is confined mainly to the lower, unsilvered, portion; the time dependence of the heat transfer rates found with cells of the type shown in Figs. 1(A) and (B) (due to the progressive electrolysis of the contents of the Dewars) is thereby markedly reduced. This has allowed the development and application of a particularly simple model which contains no arbitrary parameters [3–7,10]. At the same time, the more effective evacuation of the Dewar gap has given cells whose heat transfer coefficients have been lowered to values close to those predicted for radiation alone. This, combined with the use of Pd-alloy electrodes showing high Q_{excess}, has led to the operation of cells up to the boiling point. The evaporation of the solvent has therefore had to be taken into account in a more detailed manner [3–7,10] than in the earlier work [2] (compare eqns. (1) and (2) with eqn. (3) below).

The models for the various calorimeters can be represented conveniently by the appropriate differential equations predicting the changes with time (t/s) of the difference in temperature ($\Delta\vartheta/\text{K}$) between the cell contents and the thermostat bath. Thus, in our work up to October 1989 we have used:

$$C_{P,\text{D}_2\text{O},l}M^\circ\left[1-\frac{(1+\beta)It}{2FM^\circ}\right]\frac{\mathrm{d}\,\Delta\vartheta}{\mathrm{d}t}-C_{P,\text{D}_2\text{O},l}M^\circ\frac{(1+\beta)I\,\Delta\vartheta}{2FM^\circ}$$

change in the enthalpy content of the calorimeter

$$=\left[E_{\text{cell}}(t)-E_{\text{thermoneutral,cell}}\right]I$$

enthalpy input due to electrolysis

$$-\frac{I}{F}\left\{\left[0.5C_{P,\text{D}_2}+0.25C_{P,\text{O}_2}+0.75\left(\frac{P}{P^*-P}\right)C_{P,\text{D}_2\text{O},g}\right]\Delta\vartheta+0.75\left(\frac{P}{P^*-P}\right)L\right\}$$

enthalpy content of the gas stream

$$+Q_f(t)+\Delta QH[t-t_1]-\Delta QH[t-t_2]$$

excess enthalpy   calibration pulse

$$-k_R^0\vartheta_{\text{bath}}^3\left[1-\left(\frac{(1+\lambda)It}{2FM^\circ}\right)\right]\left\{\left[\frac{(\vartheta_{\text{bath}}+\Delta\vartheta)^4-\vartheta_{\text{bath}}^4}{\vartheta_{\text{bath}}^3}\right]+4\Phi\,\Delta\vartheta\right\}$$

time dependent   effect of radiation   effect of conduction
heat transfer coefficient

(1) (A3.7 of ref. 2)

Such an equation is naturally already based on a number of inbuilt assumptions, e.g. here the fact that heat transfer across any given element of the calorimeter surface is in a quasi-steady state and that the current efficiency for gas production is unity. Such points do not appear to be at issue. However, Wilson et al. [1] have modified the modelling somewhat by introducing second order small quantities which subsequently they show to be of such second order small character.

In eqn. (1) the term $[1 - (1 + \beta)It/2FM^{\circ}]$ allows for the change of the heavy water equivalent of the calorimeter with time: the system is "open" so that the cell contents decrease progressively with time. The term β was introduced to allow for a more rapid decrease than would be given by electrolysis alone (exposure of solid components of the cell contents, D_2O vapour carried off in the gas stream) but, as expected, the effects of β on Q_f and k_R^0 could be neglected for temperatures below $\approx 60°C$. Similarly, the term $[1 - ((1 + \lambda)It/2FM^{\circ})]$ allows for the decrease in the radiant surface area with time. In this case, the term λ must be retained, again as expected.

We take note here also of a further approximation which we have used throughout our work. We have set the term Φ, which accounts for the heat loss from the calorimeters by conduction equal to zero and have increased the radiative heat transfer coefficient k_R^0 to k_R' to allow for this assumption. In Appendix 2 [2] we showed that this leads to a small systematic underestimate of $Q_f(t)$. At the same time the random errors of the estimations are decreased markedly because the number of parameters to be fitted is reduced by one and because we do not need to make separate estimates of the radiative and conductive terms from the calibration pulse $\Delta QH(t - t_1) - \Delta QH(t - t_2)$. We note here that the system is normally calibrated using this pulse although it is also possible to do this using the perturbation produced by the "topping up" of the cells with D_2O to make up the losses due to electrolysis and evaporation [3–7,10] (this term has not been included in any of the equations used here).

We have also used throughout the thermoneutral potential at the temperature of the water bath as the reference value and we arrive at the differential equation which we used extensively in our work up to October 1989:

$$C_{P,D_2O,l}M^{\circ}\left[1 - \frac{It}{2FM^{\circ}}\right]\frac{\mathrm{d}\,\Delta\vartheta}{\mathrm{d}t}$$

$$= \left[E_{\mathrm{cell}}(t) - E_{\mathrm{thermoneutral,bath}}\right]I + Q_f(t) + \Delta QH[t - t_1]$$

$$- \Delta QH[t - t_2] - \frac{3I}{4F}\left[\frac{P}{P^* - P}\right]\left[(C_{P,D_2O,g} - C_{P,D_2O,l})\Delta\vartheta + L\right]$$

$$- k_R'\left[1 - \frac{(1 + \lambda)It}{2FM^{\circ}}\right]\left[(\vartheta_{\mathrm{bath}} + \Delta\vartheta)^4 - \vartheta_{\mathrm{bath}}^4\right] \qquad (2)$$

We point out that this equation is not to be found in ref. 2 as we have there introduced some further steps in going from eqn. (A3.7) to eqn. (A5.1).

The use of the calorimeter illustrated in Fig. 1(C) allows us to assume that the heat transfer coefficients are independent of time at the first level of approximation. We have also allowed in greater detail for the D_2O vapour carried off in the gas stream (since these cells have been used at temperatures up to the boiling point) and we have formulated the behaviour in terms of an equation which contains no arbitrary parameters:

$$C_{P,D_2O,l}\left[M° - \frac{I}{4F}\int_0^t\left(\frac{2P^* + P}{P^* - P}\right)\mathrm{d}t\right]\frac{\mathrm{d}\,\Delta\vartheta}{\mathrm{d}t}$$

$$= [E_{cell}(t) - E_{thermoneutral,bath}]I + Q_f(t) + \Delta QH[t - t_1] - \Delta QH[t - t_2]$$

$$- \frac{3I}{4F}\left(\frac{P}{P^* - P}\right)[(C_{P,D_2O,g} - C_{P,D_2O,l})\,\Delta\vartheta + L] - k'_R\left[(\vartheta_{bath} + \Delta\vartheta)^4 - \vartheta_{bath}^4\right]$$

$$(3)(A2.3 \text{ of ref. } 3)$$

However, although the major effect of the "sloping base line" has been markedly reduced, it is still present to some extent. We have therefore also used the equation with k'_R replaced by $k'_R[1 - (1 + \lambda)It/2FM°]$ (see eqn. (A4.1) of ref. 3).

METHODS OF DATA EVALUATION

The central assumption in the paper by Wilson et al. [1] is that one can assume the systems to be in a steady state at the point in time at which they are calibrated (25 990 s for the simulations given in Fig. 2) and at which the values of Q_f are to be evaluated. In point of fact there is no such steady state (neither for $\Delta\vartheta$ nor for E_{cell}) as can be seen from Fig. 2 and from Fig. 1 of the paper by Wilson et al. [1] (this figure is the same as Fig. 3A of our main paper [2]). The magnitudes of terms $M°C_{P,D_2O,l}(\mathrm{d}\,\Delta\vartheta/\mathrm{d}t)$ are in fact comparable to those of the corrections to ΔQ introduced in deriving the heat transfer coefficients $(k'_R)_1$, $(k'_R)_2$, and $(k'_R)_3$ (see below).

It is well known in many fields of research that accurate values of the parameters of the differential equations which model the systems can only be obtained by comparing the integrated forms of the equations with the experimental data. An example of such a field is that of chemical kinetics where the "steady state approximation" has frequently been used to obtain approximate values of rate constants. However, these values are well recognized as being approximate and it is also recognized that it is not feasible then to use these values to make accurate determinations of the constant terms appearing in the equations. The analogy to the application of equations (1)–(3) will be apparent.

It can be seen therefore that we need to compare the integrated forms of these differential equations with the experimental data in order to obtain accurate values of Q_f. The difficulty which presents itself immediately is that the equations are non-linear and inhomogeneous; furthermore P is a non-linear function of ϑ and
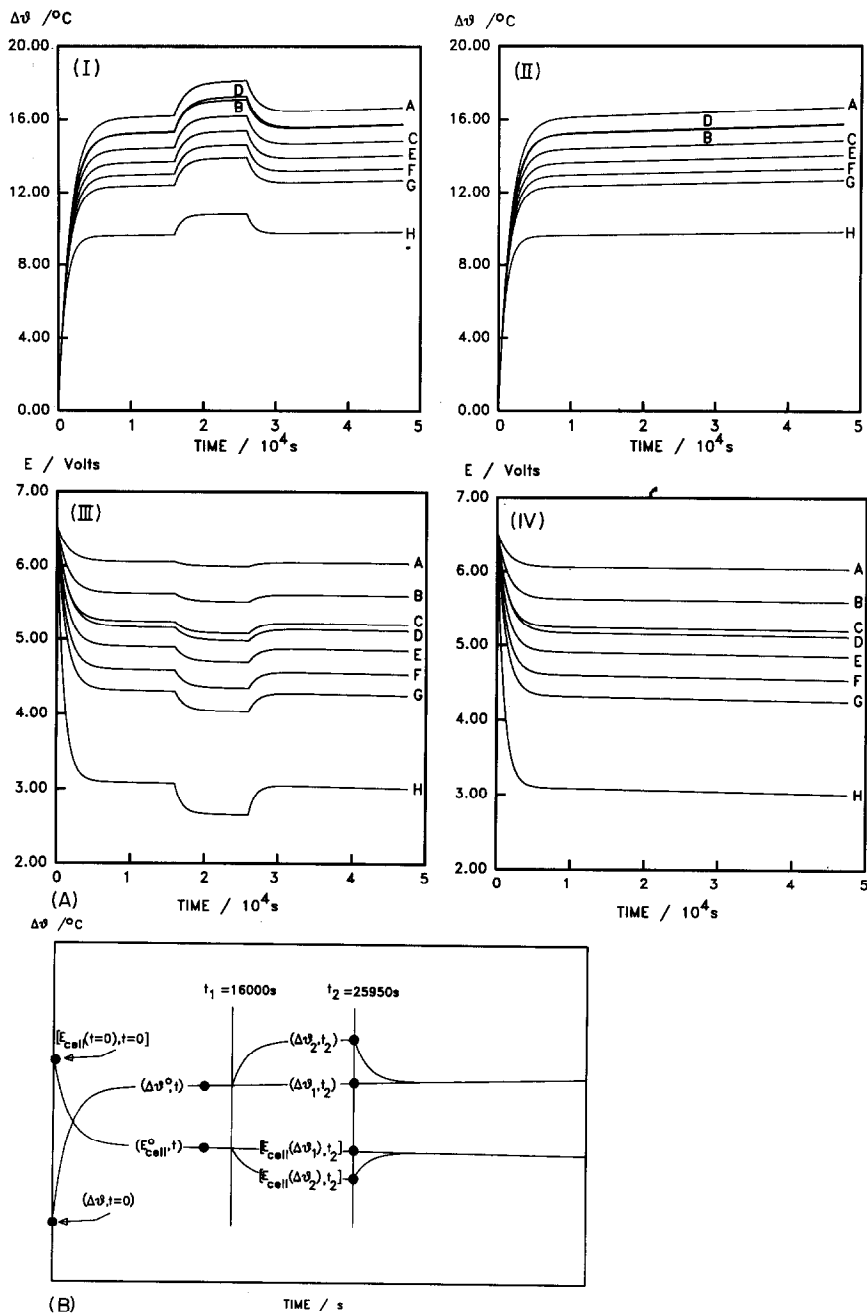
Fig. 2. (A) Simulated temperature–time and potential–time plots with and without a heater calibration pulse as a function of ψ/ϑ_{bath}: plots A = 0.03, plots B = 0.06, plots C = 0.09, plots D = 0.09 (using a linearized heat transfer coefficient), plots E = 0.12, plots F = 0.15, plots G = 0.18, plots H = 0.36. (B) Schematic diagram of the methodology used for the calculations. The points $(\Delta\vartheta_2, t_2)$; $(\Delta\vartheta_1, t_2)$; $[E_{cell}(\Delta\vartheta_1, t_2)]$; $[E_{cell}(\Delta\vartheta_2, t_2)]$; $(\Delta\vartheta = 0, t = 0)$; $[E_{cell}(t = 0), t = 0]$ were used for the calculations in Table 1 and the points $(\Delta\vartheta^\circ, t)$, (E°_{cell}, t) were used for the calculations in Appendix 4 of ref. 2.

$E_{\text{cell}}(t)$ is an unknown function of time, t. It is therefore next to impossible to develop analytical solutions of these equations (see further below and Appendices 3 and 4 of ref. 2). We have therefore used three strategies to develop "exact" methods of data evaluation:

first and foremost the comparisons of the numerical integrals of eqns. (1)–(3) with the experimental data using non-linear regression [2–6,10] (Method 2);

secondly, Kalman filtering of the data [4,6] which is also the basis of an independent evaluation of some of our data [7] (Method 4);

thirdly, point-by-point evaluation of Q_{excess} using heat transfer coefficients determined with Methods 2 and 4 [3–6,10] (Method 3).

Of these methods, 2 and 4 are undoubtedly more accurate than 3 but they do require the assumption that Q_f is constant during any given measurement cycle, a restriction which is lifted for Method 3. We note here that our preferred method of data processing is low pass filtering (such as Method 4), for reasons which will be given elsewhere [9]; we also note that some of our current work is concerned with the development of filters which allow the evaluation of the time dependence of Q_f in relaxation measurements.

Wilson et al. [1] do not deal with any of these evaluations: they regard Method 2, which was outlined in Appendix 5 of ref. 2 as "very complicated and very difficult to follow in detail". However, this method, together with low pass filtering, using, for example, the Kalman filter, is the standard method of modern data processing. The Kalman filters which have been used have been based on eqn. (3) (as well as on eqn. (A4.1) of ref. 3) which take full account of the evaporation of the solvent to within a few tenths of a percent: the assertion that we did not take this into account [1] can be seen to be incorrect; these terms were omitted in the evaluation of the results given in ref. 2 because of the restriction of the cell temperatures in those experiments (see further below). We observe that the results of the independent investigation using Kalman filtering [7] were presented to the group at GE during 1991; their omission of reference to this work shows that they also reject this method of data processing in addition to Method 2.

We are therefore reduced to examining the claim that the method put forward by Wilson et al. [1], Method 5, provides an accurate means of evaluating Q_f. The authors imply that as the results obtained by their Method 5 differ from those obtained by our own approximate method, Method 1, it is our method which must be judged to be incorrect. It is therefore necessary to make a comparison of these two techniques and we do this using simulated data. Moreover, as the results of Methods 1 and 2 can be seen to be in close accord at low and intermediate values of the input enthalpy (see Table 3 of ref. 2 and also further below) Wilson et al. [1] also cast doubts on the validity of the application of non-linear regression methods. It is therefore necessary for us to make a comparison of our own approximate and exact Methods 1 and 2 and this comparison arises naturally from the interpretation of the simulated $\Delta\vartheta$–t plots.

We have used eqn. (2) as the starting point and have assumed that the cell temperatures are sufficiently low that we can neglect the heat flow due to

evaporation of the solvent; the neglect of this term raises no new issue of principle. We have already pointed out above that the time dependence of E_{cell} cannot be specified a priori. We have therefore used the same approximation as that used in ref. 2, namely that we can carry out a Taylor series expansion of $E_{cell}(t)$ to give $E_{cell}(\vartheta)$. In order to simplify the problem as far as possible and to enhance the effects, we have here chosen this temperature to be ϑ_{bath} so that we can write

$$E_{cell}(t) = E_{cell}(t = 0) + \psi/\vartheta_{bath}\ \Delta\vartheta \qquad (4)$$

We point out, however, that in our earlier work this temperature was chosen to lie just before the application of the heater calibration $\Delta QH(t - t_1)$: $t_1 = 16\,000$ s in Fig. 2. We have also chosen the following simple values so that our calculations can readily be checked even with a pocket calculator:

$C_{P,D_2O,l} = 75$ J K^{-1} mol^{-1}
$M^\circ = 4$ mol
$E_{cell}(t = 0) - E_{thermoneutral,bath} = 5$ V
$I = 0.4$ A
$Q_f = 1$ W
$\Delta Q = 0.36$ W
$k'_R = 1.5 \times 10^{-9}$ W K^{-4}
$\lambda = 1$
$\vartheta_{bath} = 300$ K
$E_{thermoneutral,bath} = 1.54$ V
and we designate Q_1 by
$Q_1 = (E_{cell}(t = 0) - E_{thermoneutral,bath})I + Q_f$
and Q_5 by
$Q_5 = (E_{cell}(t = t_2) - E_{thermoneutral,bath})I + Q_f$
so that eqn. (2) becomes in standard form

$$\frac{d\ \Delta\vartheta}{dt} = \frac{10^{-2}}{1 - (5 \times 10^{-2}t/F)} + \frac{0.36[H(t - t_1) - H(t - t_2)]}{1 - (5 \times 10^{-2}t/F)}$$
$$- \left\{ \frac{10^{-4}\ \Delta\vartheta + 5 \times 10^{-12}[1 - (10^{-1}t/F)][(300 + \Delta\vartheta)^4 - (300)^4]}{1 - (5 \times 10^{-2}t/F)} \right\} \qquad (5)$$

for $\psi/\vartheta_{bath} = 0.03$.

Simulated plots of $\Delta\vartheta$ and E_{cell} vs. t are given in Fig. 2(A) for a range of values of ψ/ϑ_{bath} and it can be seen that eqn. (5) gives results which resemble quite closely the experimental data of Figs. 3 and 4 of ref. 2. We point out here that the values of ψ/ϑ_{bath} which apply to the experimental data are near the bottom of the range shown in Table 1. Some of the key values of $\Delta\vartheta$ and E_{cell} used in the later evaluations are given in the table.

We observe next that as far as Methods 1 and 5 are concerned we can define four heat transfer coefficients measured close to the time t_2 on Fig. 2(B) depending on the following particular assumptions [3–6,10]:

TABLE 1

Simulations of eqns. (5) and (10) and the derived values of $(k'_R)_1$, $(k'_R)_5$, Q_1 and Q_5

$-\psi I / \vartheta_{bath} / K^{-1}$	Eqn. (10)	Eqn. (5)						
	0.09	0.03	0.06	0.09	0.12	0.15	0.18	0.36
$(k'_R)_{simulation}$ /W K^{-1}	0.162	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
$(k'_R)_{simulation}$ /W K^{-4}	n.a.	1.5×10^{-9}	1.5×10^{-9}	1.5×10^{-9}	1.5×10^{-9}	1.5×10^{-9}	1.5×10^{-9}	1.5×10^{-9}
$\Delta\vartheta_2$ /K	17.327	18.178	17.148	16.221	15.383	14.624	13.932	10.820
$\Delta\vartheta_1$ /K	15.473	16.368	15.426	14.581	13.819	13.129	12.501	9.690
E_2 /V	4.981	5.995	5.511	5.080	4.694	4.346	4.032	2.645
E_1 /V	5.147	6.049	5.614	5.228	4.882	4.571	4.290	3.052
$(k'_R)_5 \times 10^9$ /W K^{-1}	0.1584	–	–	n.a.	–	–	–	–
$(k'_R)_1 \times 10^9$ /W K^{-1}	0.1942	–	–	n.a.	–	–	–	–
$(k'_R)_{1,predicted} \times 10^9$ /W K^{-1}	0.1944	–	–	n.a.	–	–	–	–
$(k'_R)_5 \times 10^9$ /W K^{-4}	n.a.	1.4635	1.4627	1.4614	1.4620	1.4601	1.4600	1.4609
$(k'_R)_1 \times 10^9$ /W K^{-4}	n.a.	1.5569	1.6518	1.7491	1.8481	1.9468	2.0468	2.6669
$(k'_R)_{1,predicted} \times 10^9$ /W K^{-1}	n.a.	1.5939	1.6896	1.7868	1.8854	1.9851	2.0858	2.7054
Q_1 /W	3.005	2.9857	2.9716	2.9618	2.9547	2.9470	2.9410	2.9290
$Q_{1,predicted}$ /W	3.0000	3.0000	3.0000	3.0000	3.0000	3.0000	3.0000	3.0000
Q_5 /W	2.4509	2.8066	2.6315	2.4746	2.3374	2.2102	2.0978	1.6045
$Q_{5,predicted}$ /W	2.4428	2.8036	2.6296	2.4752	2.3368	2.2124	2.1000	1.6048

if we allow for the change in the electrical energy input during the calibration cycle

$$(k'_R)_1 = \frac{\Delta Q - \left([E_{cell}(\Delta\vartheta)_1]_{t_2} - \{E_{cell}[(\Delta\vartheta)_2]\}_{t_2}\right)I}{\left[(\vartheta_{bath} + \Delta\vartheta_2)^4 - (\vartheta_{bath} + \Delta\vartheta_1)^4\right]} \tag{6}$$

if we allow additionally for the change in the enthalpy of evaporation of the solvent during this cycle

$$(k'_R)_2 = \frac{\begin{aligned}\Delta Q - &\left([E_{cell}(\Delta\vartheta)_1]_{t_2} - \{E_{cell}[(\Delta\vartheta)_2]\}_{t_2}\right)I\\ -&\frac{3I}{4F}\left\{\left(\frac{P_2}{P^* - P_2}\right)\left[(C_{P,D_2O,g} - C_{P,D_2O,l})\,\Delta\vartheta_2 + L\right]\right.\\ &\left.-\left(\frac{P_1}{P^* - P_1}\right)\left[(C_{P,D_2O,g} - C_{P,D_2O,l})\,\Delta\vartheta_1 + L\right]\right\}\end{aligned}}{\left[(\vartheta_{bath} + \Delta\vartheta_2)^4 - (\vartheta_{bath} + \Delta\vartheta_1)^4\right]} \tag{7}$$

if we neglect the changes in both the electrical energy input and enthalpy of evaporation of the solvent

$$(k'_R)_3 = \frac{\Delta Q}{\left[(\vartheta_{bath} + \Delta\vartheta_2)^4 - (\vartheta_{bath} + \Delta\vartheta_1)^4\right]} \tag{8}$$

and, finally, if we neglect the changes in the electrical energy input but include those for the enthalpy of evaporation of the solvent

$$(k'_R)_4 = \frac{\begin{aligned}\Delta Q - &\frac{3I}{4F}\left\{\left(\frac{P_2}{P^* - P_2}\right)\left[(C_{P,D_2O,g} - C_{P,D_2O,l})\,\Delta\vartheta_2 + L\right]\right.\\ &\left.-\left(\frac{P_1}{P^* - P_1}\right)\left[(C_{P,D_2O,g} - C_{P,D_2O,l})\,\Delta\vartheta_1 + L\right]\right\}\end{aligned}}{\left[(\vartheta_{bath} + \Delta\vartheta_2)^4 - (\vartheta_{bath} + \Delta\vartheta_1)^4\right]} \tag{9}$$

As far as the present discussion is concerned, we need to use $(k'_R)_2$ for Method 5 and to examine the significance of $(k'_R)_3$ in the evaluations based on Method 1. We will also refer to the heat transfer coefficient by Method 2 which we have designated by $(k'_R)_5$ [3–6,10] and to that determined by Method 6 as $(k'_R)_6$.

It is important to realize at the outside that Methods 1 and 5 are not the same as they lead to evaluations of the thermal balance at different times of the $\Delta\vartheta$–t transient. This should have been apparent from a comparison of Appendices 2 and 4 of ref. 2 but Wilson et al. do not refer to the latter Appendix in their paper [1].

As in that Appendix, this point can be appreciated most immediately by using the linearized form of eqn. (5):

$$\frac{d\ \Delta\vartheta}{dt} = \frac{10^{-2}}{1 - (5 \times 10^{-2}t/F)} + \frac{0.36[H(t - t_1) - H(t - t_2)]}{1 - (5 \times 10^{-2}t/F)}$$
$$- \left\{ \frac{10^{-4} + 0.162[1 - (10^{-1}t/F)]}{1 - (5 \times 10^{-2}t/F)} \right\} \Delta\vartheta \tag{10}$$

The results from a simulation based on eqn. (10) are given in the first column of Table 1: Method 5 predicts an approximate value of $(k'_R)_1$ while Method 1 predicts $((k'_R)_1 - \psi I/\vartheta_{bath})$ as was pointed out in Appendix 4 of ref. 2: needless to say, Method 1 also gives only approximate values of this parameter.

A set of data based on eqn. (5) and using a range of values $\psi I/\vartheta_{bath}$ is also given in Table 1. As can be seen, $(k'_R)_1$ is constant while $(k'_R)_6$ has the predicted values. It is important to point out here that the small deviations between the derived and predicted values of $(k'_R)_1$ and $(k'_R)_5$ are artefacts of the simulation procedure; we have used only the simplest possible forward integration method.

Values of Q_1 and Q_5 predicted using $(k'_R)_1$ and $(k'_R)_5$ are also shown in Table 1. The most immediately obvious point is that Q_5 applies to the point $t = t_2$ in Fig. 2(B) while Q_1 is evaluated at $t = 0$.

We conclude that Methods 1 and 5 are comparable but they give the thermal balance at different parts of the $\Delta\vartheta$–t transient. If Q_f is essentially constant during a measurement cycle (including the value zero for blank experiments) then it is not at all surprising that Methods 1 and 2 should give closely similar results contrary to the views expressed by Wilson et al. [1].

ERRORS AND OTHER ISSUES RAISED BY WILSON ET AL. [1]

Both our own approximate method evaluation, Method 1 [2] and that of Wilson et al., [1] Method 5, rely on making a thermal balance at a single point, t_2 in Fig. 2(B). They are therefore inevitably subject to the errors inherent in adopting such a strategy. At first sight the errors inherent in Method 1 would be expected to be dominated by the measurement of two absolute temperatures whereas Method 5 requires in addition the measurement of two cell voltages and would therefore be expected to be somewhat less accurate than Method 1.

This supposition is incorrect however because Method 1 is subject in the main to systematic errors unless due care is taken in controlling the level of electrolyte in the cells at the point at which the measurements are taken; by implication, Method 5 will be subject to the same systematic errors. We illustrate this point by the results of 33 sets of calibration cycles, shown in Fig. 3(A), a typical cycle being shown in Fig. 3(B) (Fig. 5A of ref. 2; Fig. 3(A) was not given in ref. 2). This variability has been recognized by other authors e.g. refs. 11 and 12 and Wilson et al. [1] reiterate the assertion that measurements can only be made to 5%–10%
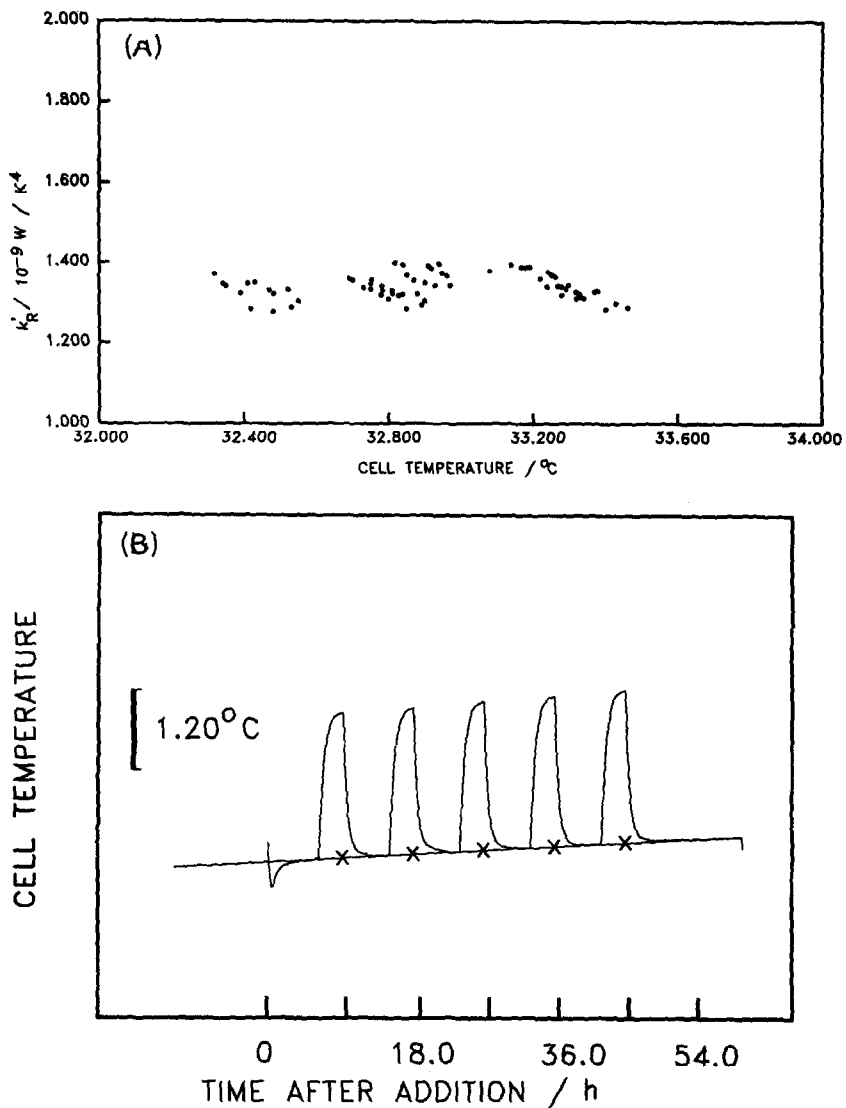
Fig. 3. (A) Plot of the heat transfer coefficients for multiple sets of calibration cycle experiments as a function of cell temperature. (B) A typical set of calorimeter calibration cycles made at 9, 18, 27, 36 and 45 h after the addition of D_2O (0.1×10 cm Pd electrode polarized at 0.1 M LiOD at a current density of 64 mA cm^{-2}). (C) The derived heat transfer coefficients for 14 calibration cycles as a function of time after the addition of D_2O. (D) Superposition of 165 derived heat transfer coefficients determined in 33 sets of calibration cycles for a single cell. The superposition was made at the 27 h calibration point and demonstrates the precision of $\sigma_R = 0.155\%$ in determining the actual coefficient at the remaining points.
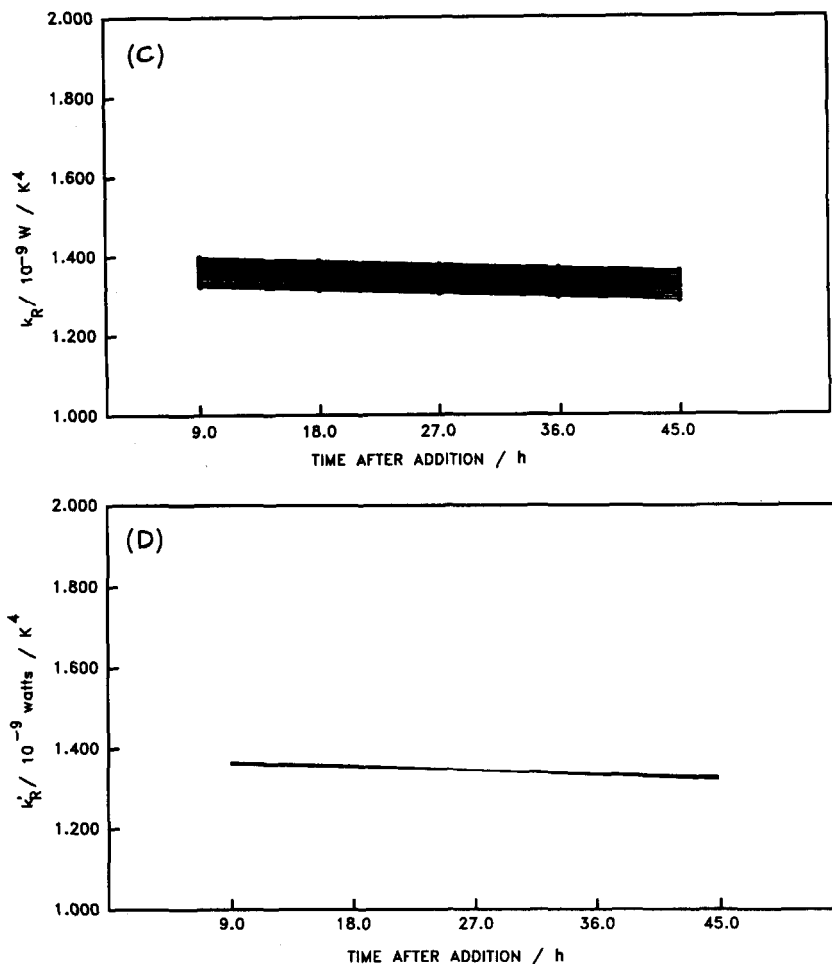
Fig. 3. (continued).

precision with this type of calorimetric technique. It is well known that isoperibolic calorimetry is capable of an accuracy of 1%–2% even without paying special attention to problems which limit the accuracy; we contend that we have taken special steps in this regard.

That the variability that we have observed in our measurements is systematic rather than random is shown by Fig. 3(C) (Fig. 5C of ref. 2); superposition of these plots at the central calibration point shows that the residual standard deviation is only 0.155%, see Fig. 3(D) (Fig. 5D of ref. 2).

The variability is due to changes in the level of electrolyte in the calorimeters, i.e. of the term $[1 - (1 + \lambda)It/2FM°]$ in eqn. (5) and the related equations and must be taken into account in accurate methods of data analysis. The cause of the

variability has also been correctly identified by others [11] but, to the best of our knowledge, has so far only been allowed for in the work reported by us, e.g. in ref. 2.

The question naturally is how can such an objective be achieved? The precise control of the level of electrolyte in routine work is hardly feasible (but, naturally, such precise control needs to be achieved for measurement cycles which are to be evaluated in detail). The answer lies in making the term $[1 - (1 + \lambda)It/2FM°]$ (or of other equivalent parameters) part of the evaluation and this in itself dictates the strategy that the whole of the $\Delta\vartheta$–t and E_{cell}–t transients be fitted to the integrated forms of the differential equations which model the calorimeters i.e. it dictates the use of methods such as Methods 2 and 4. It is not surprising that such methods can give precise results as a matter of routine.

The information on this issue which was contained in our original paper [2] and in the related papers has been ignored by Wilson et al. [1]. They have also ignored the fact that we showed that it is possible to achieve at least 99% heat accuracy by the methods we have used (Table 2 of ref. 2); we have never claimed an accuracy of better than 1% or 1 mW, whichever is the greater. They also do not discuss the fact that even on the basis of their own evaluations the excess enthalpy for a 0.2 cm diameter × 10 cm length Pd cathode polarized at 128 mA cm^{-2} has reached $\approx 50\%$ of the enthalpy input after 15 days of polarization (data taken from Fig. 4C of ref. 2). Presumably they believe that the errors have now reached 50% to explain away these effects? It should be noted that these enthalpy outputs are of the order 4 W cm^{-3} or ≈ 42 W mol^{-1} of Pd and that over the duration of the experiment shown the total enthalpy released is of the order 4 MJ cm^{-3} or 42 MJ mol^{-1} of Pd, which hardly lies in the province of Chemistry.

Wilson et al. should have set out their scheme of calculation for this series of experiments set out in Figs. 4A, B and C of our paper [2]. Of this series, Fig. 4C would have been the most reasonable choice (excess enthalpy in the middle range of those reported in ref. 2; cell temperature in the acceptable range). The excess enthalpies generated in the experiments described by Figs. 3A, B and and C (and which have been used by Wilson et al. for part of their analysis leading to Table 1 of ref. 1) are too low to allow reliable calculations to be made from data points read from these graphs (these graphs and the data diskettes have been claimed as the property of, and are in the hands of, NCFI and the University of Utah). This set of figures was included to illustrate the behaviour of the systems at the low end of excess enthalpy generation. It was an unfortunate choice; the example should have been for the polarization at the same current density (64 mA cm^{-1}) either of shorter electrodes in the same calorimeter or of the given electrode (0.4 cm diameter × 10 cm length) in a calorimeter of larger diameter. As it is, the temperatures are too high to allow the application of methods such as 1 and 5. We observe that Wilson et al. [1] have chosen the most unsuitable example for their detailed calculation, namely Fig. 3A of ref. 2 (low excess enthalpy, high cell temperature) and their scheme of calculation inevitably magnifies the errors (multiplication and division by the differences between two large quantities).

TABLE 2

Comparisons of the values of the heat transfer coefficient calculated by Wilson et al. [1] with the lower bound $(k'_R)_6$ for the data in Figs. 3A–C of ref. 2; comparison of Q_f in ref. 1 with that derived using the lower bound $(k'_R)_6$ and the values in ref. 2

Fig. in ref. 2	$k'_R \times 10^9$/W K^{-4}	Q_f/W	$(k'_R)_6 \times 10^9$ /W K^{-4} (lower bound)	Q_f/W	Q_f/W [2]
	Wilson et al. [1]		This paper		
3A	0.81	−0.43	0.94	0 (assumed)	0.158
3B	(0.96?) [a]	(−0.48?) [a]	n.a.	0.100	0.178
3C	0.92	−0.37	n.a.	0.528	0.372

[a] Note to the Editor: these values are illegible on the copy of the draft paper in our possession.

That the analysis of Wilson et al. [1] is incorrect, quite apart from its lack of accuracy (it leads to double subtraction errors, see below), can be seen by comparing their calculation of k'_R with that of $(k'_R)_6$ using Method 6. In this method we assume that $Q_f = 0$ at the time just before the application of the calibration pulse (Fig. 1 of ref. 1 or Fig. 3A of ref. 2). We ignore completely the use of this pulse and use eqn. (2) to estimate $(k'_R)_6$; as can be seen from Table 2 this lower bound for k'_R is in fact much larger than the value deduced by Wilson et al. [1], which shows that their calculation is subject to a gross error. The use of this value of $(k'_R)_6$ for the data in Figs. 3B and 3C of our paper [2] gives the excess enthalpies shown in Table 2, not the negative enthalpies derived by Wilson et al. [1] (which contravene the laws of thermodynamics). We point out, however, that in the absence of a proper calibration these values of the excess enthalpies are inevitably inaccurate. We point out furthermore that a somewhat similar calcula-tion in the independent evaluation of a different data set (but based on the application of Kalman filtering and using eqn. (3) [7]) has also given excess enthalpy which increases progressively with time. We emphasize again that a proper analysis must rely on the comparison of the integrated equations with the experimental data sets (such as Methods 2 and 4) and these comparisons must be based on the differential equations which take full account of evaporative cooling, for example eqn. (3) (see further below). As we have noted above, we restricted exact calculations in ref. 2 to those cases where the details of evaporative cooling could be neglected and the values of Q_f quoted for Figs. 3A–C and Figs. 4A–C remained estimates rather than exact values.

We note here that we agree with the discussion by Wilson et al. [1] of the effects of evaporative cooling and our own calculations of these effects (based on readings taken from the published figures [2]) are given in columns 6–8 of Table 3.

We draw attention here to the fact that the E_{cell}–t plots in Figs. 3 and 4 of ref. 2 have been displaced by one data point (300 s) to longer times than the $\Delta\vartheta$–t plots by the plotting routines used to generate these figures. We have corrected for

TABLE 3

Corrections to the data in Figs. 3A–C and Figs. 4A–C of ref. 2 to allow for changes in the evaporative cooling terms in eqn. (7) due to the resistive heater calibration pulse; corrections to Q_f to allow for the use of $(k'_R)_2$ instead of $(k'_R)_1$ or $(k'_R)_3$ as well as for the heat flows due to evaporation and the heating of the cell contents

Fig. in ref. 2	$\Delta\vartheta_2$ /K	$\Delta\vartheta_1$ /K	P_2 /bar	P_1 /bar	Evaporative heat flow at $\Delta\vartheta_2$ /W	Evaporative heat flow at $\Delta\vartheta_1$ /W	Correction to Q_f to allow for the use of $(k'_R)_2$ /W	Credit to allow for heating of cell contents /W	Q_f given in ref. 2 /W	Corrected Q_f /W
3A	333.51	331.82	0.193	0.178	−0.077	−0.070	−0.103	+0.014	0.158	0.139
3B	335.67	334.04	0.212	0.197	−0.087	−0.079	−0.131	+0.014	0.178	0.140
3C	341.37	339.74	0.272	0.254	−0.124	−0.112	−0.228	+0.018	0.372	0.274
4A	323.09	321.17	0.118	0.113	−0.042	−0.040	−0.032	+0.011	0.736	0.755
4B	325.33	323.44	0.132	0.121	−0.048	−0.044	−0.039	+0.013	0.888	0.906
4C	327.70	325.84	0.148	0.135	−0.055	−0.050	−0.055	+0.014	1.534	1.543

this displacement in drawing up Tables 2 and 3. We also draw attention to the need to correct for the heating of the cell contents (the term $C_{P,D_2O,l}[1 - It/2FM°](d\,\Delta\vartheta_1/dt)_{t=t_2}$ in column 9 of Table 3) when the smaller terms in the estimation of Q_f are taken into account. The difference $C_{P,D_2O,l}[1 - It/2FM°][(d\,\Delta\vartheta_2/dt)_{t=t_2} - (d\,\Delta\vartheta_1/dt)_{t=t_2}]$, although detectable, is too small to be taken into account in evaluating the heat transfer coefficients using Methods 1 or 5.

The major correction term estimated by Wilson et al. [1], that due to their correction of ΔQ due to the change induced by the heater pulse on the cell potential, is, however, not applicable. As we have shown above and in Appendix 4 of ref. 2, that term has already been taken into account in estimating Q_f using $(k_R')_3$ as given by Method 1. The scheme of calculation adopted by Wilson et al. [1] therefore leads to a double correction of k_R' for the effects of changes of the cell potential. It is not surprising therefore that the magnitudes of the corrections to Q_f calculated by Wilson et al. [1] are precisely of the order expected for such a double subtraction. The values of k_R' derived are too low (as the authors themselves remark) and the authors also conclude that the cells are markedly endothermic for the conditions represented by Fig. 3A of ref. 2, a condition which evidently contravenes the laws of thermodynamics.

That the conclusions reached by Wilson et al. are untenable is shown by the simulation of the $\Delta\vartheta-t$ curves using their derived parameters in eqn. (2) (Fig. 4). These simulations demonstrate clearly the inadequacy of using a single point calculation to predict the observed response of these calorimeters; it is pointed out again here that one must use the fully integrated form of the differential equations for such predictions. We regard it as being most important that such checks be made routinely in any further development of the calorimetry of electrode reactions and note that Method 4, Kalman filtering, has a special advantage in that it produces comparisons of the experimental data and of the simulation using the derived parameters as an intermediate step in the calculations.

Instead of exploring the causes of their conclusions, Wilson et al. [1] discuss the validity of our "blank" experiments and their discussion is again largely based on their misinterpretation of our Method 1. They maintain quite correctly that this method could not be expected to give results in close accord with those of Method 4 at high enthalpy inputs. This is indeed apparent from our own results for Pd cathodes polarized in D_2O, given in Table 3 of ref. 2. The explanation is that the "blank" experiments have been incorrectly described in the footnotes of Table 4. It was our uniform practice at that time to reduce the lengths of our cathodes to 1.25 cm at high enthalpy inputs (e.g. Table 3 of ref. 2). For these blank experiments we still followed the manner of presentation first given in our preliminary publication [13] of subsequently rescaling the results to electrodes of 10 cm length. The erroneous results of cells operating above the boiling point is explained by this rescaling of the data.

We return finally to the question of the applicability of the various heat transfer coefficients $(k_R')_1-(k_R')_5$ described above. We have found in our more recent work
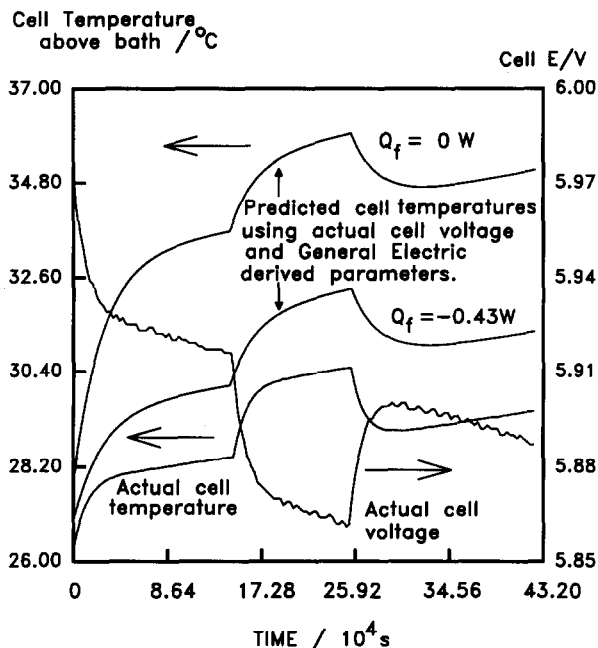
Cell Temperature
above bath /°C

Cell E/V

Fig. 4. Comparison of the data shown in Fig. 3A of ref. 1 (two lower plots) with simulations of the temperature response using the given cell voltage and the parameters derived by Wilson et al. [1]: $k_R' = 0.81 \times 10^{-9}$ W K^{-4}, $\Delta Q = 0.24$ W; and (top plot) $Q_f = 0.0$ W or (bottom plot) $Q_f = -0.43$ W.

using cells of the type shown in Fig. 1(C) that a long term balance of the enthalpy generated in "blank" experiments (Pt cathodes polarized in H_2O or D_2O; Pd cathodes polarized in H_2O) is only achieved when using the heat transfer coefficients derived by non-linear regression fitting, Method 2 [3–6,10]. It is of interest that these heat transfer coefficients are closely similar to those derived by Kalman filtering, Method 4. The use of $(k_R')_1$ or $(k_R')_2$, eqns. (6) and (7), indicates endothermic operation of these cells, which is clearly impossible. It is also of interest that, notwithstanding the endothermic operation of these cells when using $(k_R')_1$ or $(k_R')_2$, the use of these coefficients nevertheless shows that Pd-alloy cathodes polarized in D_2O generate excess enthalpy. The fact that the heat transfer coefficients $(k_R')_1$ and $(k_R')_2$ are evidently too small indicates that the steady state approximation is inapplicable for reasons which we do not as yet understand. It is certain, however, that the inapplicability of the approximation leads to some further forms of "double subtraction error". However, we have not investigated this because precise methods of data evaluation are available; for the work reported in ref. 2 we used $(k_R')_3$ as an initial value in the non-linear regression procedure which leads to precise values of Q_f.

CONCLUSION

The critique presented by Wilson et al. [1] is based largely on a misreading and misrepresentation of the information contained in ref. 2. We are unable to make any judgement of the authors' own work on the subject since the paper contains no experimental details or results. We observe that some of our own work has now been subjected to an independent analysis [7] and indeed we made it a condition of our continuing work on this topic after October 1989 that this should be done. It would be useful if the experimental work of Wilson et al. [1] could be made available for such independent scrutiny. This would allow the application of advanced data processing methods to the results, and, at the very least, lead to a clear definition of the experiments carried out.

GLOSSARY

$C_{P,O_2,g}$	Heat capacity of O_2, J K^{-1} mol^{-1}.
$C_{P,D_2,g}$	Heat capacity of D_2, J K^{-1} mol^{-1}.
$C_{P,D_2O,l}$	Heat capacity of liquid D_2O, J K^{-1} mol^{-1}.
$C_{P,D_2O,v}$	Heat capacity of D_2O vapour, J K^{-1} mol^{-1}.
E_{cell}	Measured cell potential, V.
$E_{cell,t=0}$	Measured cell potential at the time when the initial values of the parameters are evaluated, V.
$E_{thermoneutral,bath}$	Potential equivalent of the enthalpy of reaction for the dissociation of heavy water at the bath temperature, V.
F	Faraday constant, 96484.56 C mol^{-1}.
g	Gas phase.
H	Heaviside unity function.
I	Cell current, A.
k_R^0	Heat transfer coefficient due to radiation at a chosen time origin, W K^{-4}.
(k_R')	Effective heat transfer coefficient due to radiation, W K^{-4}.
l	Liquid phase.
L	Enthalpy of evaporation, J K^{-1} mol^{-1}.
$M°$	Heavy water equivalent of the calorimeter at a chosen time origin, mol.
P	Partial pressure, Pa; product species.
$P*$	Atmospheric pressure, Pa.
Q_f	Rate of generation of excess enthalpy, W.
$Q_f(t)$	Time dependent rate of generation of excess enthalpy, W.
t	Time, s.
ΔQ	Rate of heat dissipation of calibration heater, W.
$\Delta \vartheta$	Difference in cell and bath temperature, K.
$\Delta \vartheta'$	Difference in cell and bath make-up stream temperature, K.
ϑ	Absolute temperature, K.

ϑ_{bath}	Bath temperature, K.
ϑ_0	Cell temperature at $t = 0$, K.
λ	Slope of the change in the heat transfer coefficient with time.
Φ	Proportionality constant relating conductive heat transfer to the radiative heat transfer term.
ψ	Slope of the change of cell potential with temperature, $V\ K^{-1}$.

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