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THE CALORIMETRY OF ELECTRODE REACTIONS AND MEASUREMENTS OF EXCESS ENTHALPY GENERATION IN THE ELECTROLYSIS OF D₂O USING Pd-BASED CATHODES

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Introduction

In the period since March 1989 there has been much comment and doubt expressed concerning the accuracy of the calorimetric techniques that we adopted to demonstrate the presence of excess enthalpy generation during the electrolysis of D₂O solutions at palladium-based electrodes. ⁽¹⁻⁶⁾ As it is only the end of the second year of research in this area, it seems appropriate at this point in time to summarize what we have actually done and to comment on the work in progress.

We point out at the start that such calorimetric measurements are not trivially simple since there are many variables and details of the calorimeter design that have to be considered. Many of these variables and design details do not play a significant role in the determination of the thermal outputs of the calorimeters, while a few of the factors are critically important. This was well-known before the publication of our preliminary note ^(1,2) but in view of the often repeated criticisms it became necessary to establish this conclusion by further extensive investigations of the effects of all the pertinent variables on the behavior of our calorimetric systems. While it is certainly true that these investigations influenced the development of the calorimeter design and methods of data analysis, the conclusions which we reached in March 1989 have not been markedly affected.

One factor which was of key importance to our choice of calorimeter design was the variability of the magnitudes of the rates of excess enthalpy generation and the sensitivity of these rates to a wide range of system variables so that a large number of experiments were required (and this need continues!). In consequence it has been necessary to use low-cost

calorimeters. Most importantly, it has always been evident that each experiment be carried out for very long times: the minimum time for a single experiment has been three months.

In this paper we outline first of all the general considerations which influenced our choice of calorimeter and then describe the evolution of the design since October 1989. We go on to discuss the methodology which we have adopted to obtain accurate thermal balances for the cells. In this discussion we pay particular attention to a number of issues which have been raised repeatedly and which are important to the understanding of the limits of accuracy as well as the sensitivity of the measurements with such calorimeter designs; some of these issues have not yet been adequately described in the literature but are of crucial importance to measurements of excess enthalpy generation at very low enthalpy inputs. These measurements are part of our ongoing program, this part being aimed at the understanding of the reality or otherwise of a “threshold” for the onset of excess enthalpy generation. In the final section we give an outline of some of our recent measurements at the opposite extreme of intermediate to high current densities. The excess enthalpy generated under such conditions is so high that precise characterization of the calorimeters proves to be unnecessary since, in the limit, heat transfer from the cells is dominated by evaporation of the solvent.

Factors Influencing the Design of Electrochemical Dewar Calorimeters: Early Designs.

In the experiments reported to date, we have been concerned mainly with the electrode reactions



in which O_2 gas is continuously evolved at the anode surface while D_2 gas is evolved at the cathode following the charging of the lattice with deuterons. The possible sources of heat generation in the cell will then be due to reactions (i) and (ii), any catalytic recombination of deuterium and oxygen in the cell, any other chemical reactions occurring in the solution or at the electrode surfaces (or at the surfaces of any other cell components), Joule heating of the electrolyte solution and any excess enthalpy generation in the metal lattice.

The total enthalpy generation in the cell will be coupled to heat flow into and out of the calorimeter through the radiant surfaces and through the thermally conductive components of the cell at the top of the calorimeter. The sources of heat generation are localized and the temperature fluctuations due to these localized sources are dissipated by the decay of eddies; we have pointed out that the simplest method of efficiently reducing these non-uniformities at low cost is to build calorimeters that are in the shape of long cylinders, and the first generation calorimeter was of the type shown in Fig. 1. In such calorimeters, enthalpy generation at or in the

electrodes is uniform in the axial (z) direction. The gas evolution reactions (i) and (ii) ensure that the thermal equilibration of temperature in the cell will then be due to convective stirring by the eddies developed in the electrode boundary layers and their subsequent relaxation into the bulk of the solution. We have demonstrated that this occurs rapidly, and that the rate of radial mixing is about one order of magnitude faster than total mixing in the axial direction. We have reported that for intermediate to high rates of electrolysis of H₂O or D₂O (current densities in the range of about 50-2000mA cm⁻²; cell currents 200-1600mA) the gas evolution gives rise to radial mixing on a time scale on the order of ~3s and axial mixing on a scale of about ~20s. Axial gradients in temperature therefore are never established, and the thermal relaxation times ($\tau \sim M_0/4k'_R\theta_{\text{bath}}^3$) of these calorimeters are known to be ~1 hour; the calorimeters behave as well-stirred tanks (uniform temperature).

We have drawn a number of conclusions regarding the design criteria of these calorimeters from consideration of the likely sizes of the diffusing thermal eddies and their rate of relaxation into the solution. In summary, we have concluded that it is necessary to decrease the diameter of the cells with respect to the length and to minimize the total volume as far as possible. Furthermore, it is necessary to scale the radiant surface area of the calorimeter so that sufficiently large values of the differences in temperature between the cell contents and the bath are established so as to allow sufficiently accurate measurements to be made. In this way we can also minimize the effects of the fluctuations and achieve an adequate signal/noise for the measurement of the sought effects. The likely maximum values of the errors encountered in the enthalpy generation in this type of calorimeters have been reported elsewhere ⁽⁴⁾.

In our estimation many other workers have not given careful consideration to these factors and conclusions have been reached based on experimental results that therefore are subject to excessive sources of systematic and random errors. This is true especially of conclusions regarding the accuracy of such measurements which, needless to say, are strongly affected by the scaling of the electrodes and Dewar cells (other factors are discussed below).

The evolution of our own calorimeter design has followed an iterative program so as to establish that measurements of the excess enthalpy generation are large compared to the systematic and random errors and this program of work is still in train. The measurements made with the generation of calorimeters used in the collection of data up to the report contained in the first full paper ⁽⁴⁾ Fig. 1, were shown to be primarily dependent on four independent parameters: (1) the heat transfer coefficient of the cell (at a chosen time of the experiment), (2) the water (heavy water) mass equivalent of the cell, (3) a parameter to allow for the time dependency of the contents of the cell, and therefore the time dependency of the heat transfer coefficient, and (4) the magnitude of any excess enthalpy generation. The understanding and application of the parameter (3) has, in most instances, been ignored or misused, eg^(7,8) (see further below) and, as a result, the natural evolution of calorimetric studies of the electrochemical reactions has been severely impeded.

Further Evolution of the Calorimeter Design

In late 1989 we adopted a new type of calorimeter for some sets of experiments. The change in design was adopted so as to remove most of the effects of changes in the cell contents on the measurements (parameter (3)). A schematic of this cell is shown in Fig. 2. The design is closely similar to that of the earlier cells, Fig. 1, except for one important change: the silvering of the top portion ensures that heat transfer to the surrounding water bath is dominated by radiation through the lower unsilvered portion. In this way we can ensure that the heat transfer coefficient remains substantially constant during a given measurement cycle providing the fall of the level of electrolyte in the cell due to the combined effects of electrolysis and evaporation is confined to the upper silvered section of the Dewar. The slope of the temperature-time base-line is thereby markedly reduced.

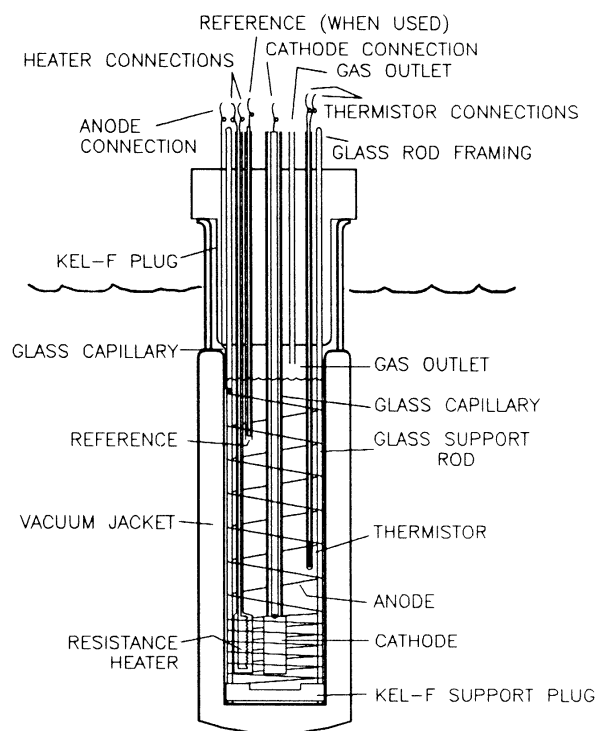


Fig. 1. Original Dewar calorimeter.

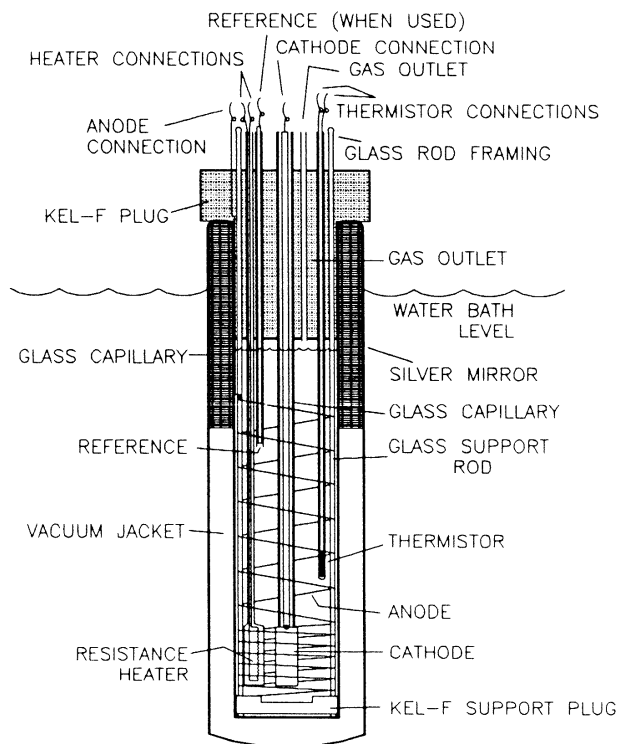


Fig. 2. Silvered Dewar calorimeter.

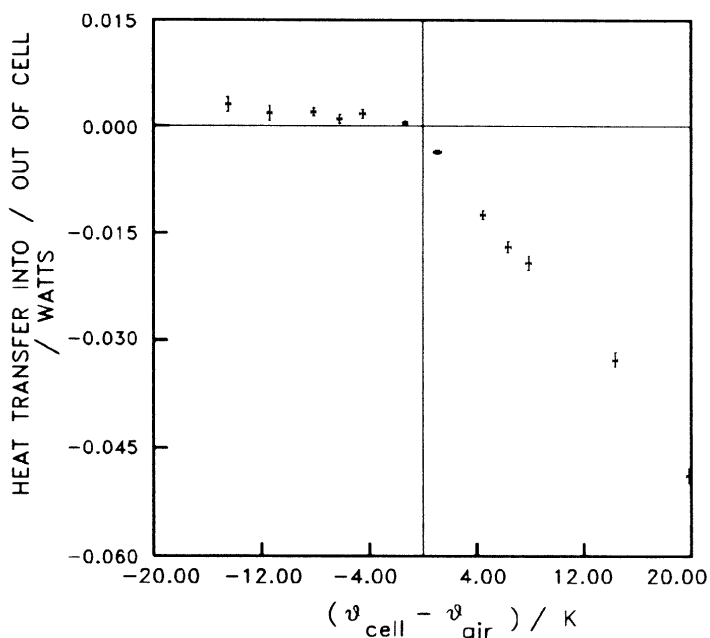


Fig. 3. Plot of rate of heat transfer vs. difference in cell and ambient temperatures.

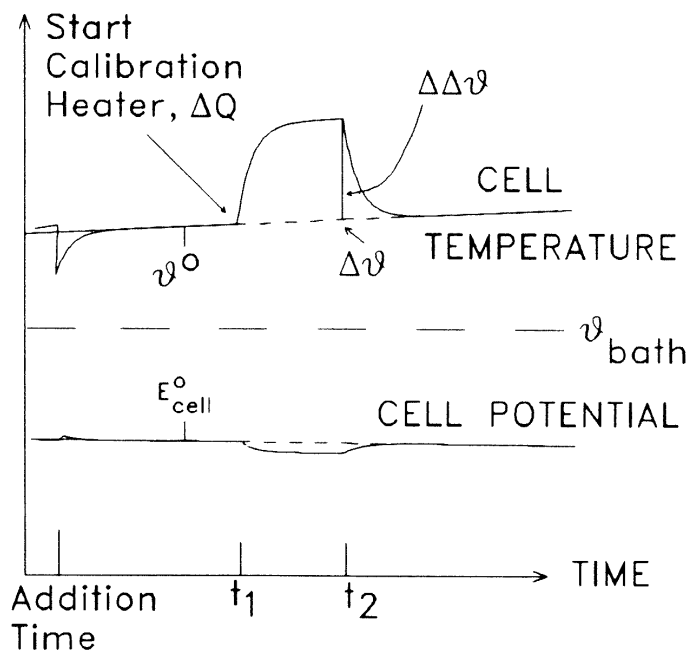


Fig 4. Schematic of methodology used in calibrating the various calorimeters.

The heat transfer coefficients determined for these new cells is close to the values calculated from the Stefan-Boltzmann coefficient and the radiant surface area. The larger values determined for the cells used in our earlier work ⁽¹⁻⁶⁾ were due to conduction across the “vacuum gap” due to imperfect evacuation of the cells ie, the conduction path was in parallel to the radiative path not to the air through the top of the cell (see further below).

Further simple changes in the cell design are being investigated at the present time. The objective of these changes is to ensure a more complete sealing of the cell contents and a restriction of air circulation within the closure of the top of the Dewar.

Other Experimental Considerations

Numerous experimental variables must be controlled so as to reduce the systematic and random errors which can affect the open-cell calorimetric experiments. Some of these variables are self-evident such as the accurate calibration of thermistors and of heater powers used to derive heat transfer coefficients. The effects of other variables is less obvious. Thus, for example, it is not well understood that it is necessary to control the ambient room temperature (and, to a lesser extent humidity) in order to achieve close control of the temperatures of the water baths. In our own work we achieve ± 0.003 degree although the experiments are scaled so as to never require better than ± 0.01 degree.

One statement which has been frequently made about the precision of our measurements is that this is markedly reduced by lack of control of heat transfer by conduction through the top of

the cell. That this statement is erroneous is shown by the data in Fig. 3 (note also that we control the room temperature to $\pm 1^\circ$). Thus Fig. 3 relates the heat flow out of or into the cell to the difference between the cell and air temperature (according to whether this is negative or positive). The direction of heat flow in these measurements was controlled by changes in the temperature of the water bath (it should be noted that the cell temperature is close to that of the bath in these experiments). The reason for the change in magnitude of the heat transfer coefficient is almost certainly due to increased air circulation in the glass tubes passing through the Kel F plug. However, the effects of these conductive contributions are in any event quite minor for appreciable differences between the cell and bath temperatures. If necessary, the effect of conduction through the top of the cell can be eliminated by adjusting the cell to the room temperature (using auxiliary cooling of the water bath) but the contribution can also be calculated to better than 0.1mW. We have shown elsewhere that the effects of conduction can in any event be taken into account by defining a modified radiative heat transfer coefficient which is derived from appropriate calibrations of the cell using a resistive heater. This procedure leads to an underestimate of the heat transfer from the cell.: we have always followed procedures which lead to such systematic underestimates but these effects can be corrected for if this is required.

Consideration of Various Methods for the Determination of Heat Transfer

The determination of the heat transfer coefficients and subsequently the rate of the rates of enthalpy generation in these open electrochemical systems is complicated, as mentioned above, by the fact that the contents of the cell change with time; this is true particularly for the results taken completely with unsilvered Dewars⁽¹⁻⁶⁾. In such a situation, it is clear that a true steady state cannot be attained inside the cell. This would require that $E_{\text{cell}}(t) = \text{constant}$ as well as $\theta(t) = \text{constant}$, and this is never observed. The values of the heat transfer coefficients, therefore, determined from the experimental data depend on the nature of the assumptions underlying the evaluations. Some of our colleagues and associates have argued that it is possible to assume a quasi-steady state and to set $\frac{d\Delta\theta}{dt} = 0$ in the non-linear inhomogeneous differential equations which describe the appropriate “black-box” models of the calorimeter. This risky assumption of course is motivated by the fact that the evaluation of k_R' and $\{E_{\text{cell}}(t) - E_{\text{thermoneutral,bath}}\}I + Q_f$ is considerably simplified since one can then ignore the water/heavy water mass equivalent M^0 of the cell (the total amount of material in the cell). If we also assume the value of the excess enthalpy $Q_f(t)$ (if this term is present) to be independent of the experimental conditions and further neglect the rate of change in the evaporation of the solvent one determines a value of the heat transfer coefficient which we denote by

$$(k_R')_1 = \frac{\Delta Q - \{[E_{\text{cell}}(t)]_1 - [E_{\text{cell}}(t)]_2\}I}{[(\theta_{\text{bath}} + \Delta\theta_2)^4 - (\theta_{\text{bath}} + \Delta\theta_1)^4]} \quad (1)$$

where the definitions of the terms are given in Fig. 6. If we treat the change in the evaporation term in the same way as the change in the cell potential, we obtain by analogy to (1) the heat transfer coefficient

$$(k'_R)_2 = \Delta Q - \{[E_{\text{cell}}(t)]_1 - [E_{\text{cell}}(t)]_2\}I$$

$$\frac{-3I}{4F} \left\{ \left(\frac{P_2}{P^* - P_2} \right) [(P_{\text{P,H}_2\text{O,v}} - C_{\text{P,H}_2\text{O},\ell})\Delta\theta_2 + L] \right.$$

$$\left. - \left(\frac{P_1}{P^* - P_1} \right) [(C_{\text{P,H}_2\text{O,v}} - C_{\text{P,H}_2\text{O},\ell})\Delta\theta_1 + L] \right\}$$

$$\frac{}{[(\theta_{\text{bath}} + \Delta\theta_2)^4 - (\theta_{\text{bath}} + \Delta\theta_1)^4]} \quad (2)$$

where P_1 , P_2 , and P^* are the vapor pressures at the two temperatures and under standard conditions, respectively, and L is the latent heat of evaporation. We regard these two estimates of the heat transfer coefficients to be lower limits.

We have argued that the change in the electrode potential due to the heater pulse ΔQ should not be included in estimating the heat transfer coefficient since the value of k'_R derived by excluding this change is then used to estimate $E_{\text{cell}}(t) - (E_{\text{thermoneutral,bath}})I + Q_f$. We obtain the heat transfer coefficient

$$(k'_R)_3 = \frac{\Delta Q}{[(\theta_{\text{bath}} + \Delta\theta_2)^4 - (\theta_{\text{bath}} + \Delta\theta_1)^4]} \quad (3)$$

In deriving this heat transfer coefficient we have also included any change of the term $\frac{-3I}{4F} \left\{ \left(\frac{P_2}{P^* - P} \right) [(P_{\text{P,H}_2\text{O,v}} - C_{\text{P,H}_2\text{O},\ell})\Delta\theta + L] \right\}$ with any change in $\Delta\theta$ caused by the application of a calibration pulse ΔQ . If we were to split off the change in this quantity with $\Delta\theta$ from the variation of $E_{\text{cell}}(t)$ with $\Delta\theta$, then by analogy with equations (1) and (2) we would define a heat transfer coefficient

$$\Delta Q - \frac{-3I}{4F} \left\{ \left(\frac{P_2}{P^* - P_2} \right) [(P_{\text{P,H}_2\text{O,v}} - C_{\text{P,H}_2\text{O},\ell})\Delta\theta_2 + L] \right.$$

$$(k'_R)_4 = \frac{- \left(\frac{P_1}{P^* - P_1} \right) [(C_{\text{P,H}_2\text{O,v}} - C_{\text{P,H}_2\text{O},\ell})\Delta\theta_1 + L] \left. \right\}}{[(\theta_{\text{bath}} + \Delta\theta_2)^4 - (\theta_{\text{bath}} + \Delta\theta_1)^4]} \quad (4)$$

We have regarded $(k'_R)_3$ as an upper limit.

Finally, we have estimated another $(k'_R)_5$ based on the application of non-linear regression fitting of the appropriate “black-box” model of the calorimeters to experimental data derived using these calorimeters. This regression fitting procedure naturally also yields estimates of M^0 and Q_f as well as the error limits for all parameters.

The most straightforward way of testing the applicability of the various heat transfer coefficients is the simulation of θ - t curves using the various models, the known values of the various parameters, values of $E_{\text{cell}}(t)$ determined directly from the operating cells and choosing values of M^0 and $(k'_R)_5$ derived by the application of the non-linear regression fitting procedure.

We then in turn use equations (1)-(4) to estimate the heat transfer coefficients which are based on the various approximations and we can reapply the non-linear regression procedure to the data simulated with these coefficients, Fig. 5. The divergence between the various heat transfer coefficients is also brought out clearly by Fig. 6 which is based on simulated data alone and includes the effects of the heater calibration pulse. It can be seen that the values $(k_R')_1$ and $(k_R')_2$ are incorrect. The main cause in the invalidity of the steady state approximation is that the relevant differential equation must be integrated across the whole of the time region to give a correct account of the shape (and especially the amplitude) of the θ -t profile due to the heater calibration pulse.

The results confirm our belief that $(k_R')_1$ and $(k_R')_2$ are lower limits while $(k_R')_3$ is an upper bound. $(k_R')_4$ may be an overestimate or underestimate depending on the conditions but we have not pursued this question further since any of the values $(k_R')_1$ - $(k_R')_4$ can be used as starting points for the non-linear regression fitting; the question of why the use of $(k_R')_1$ - $(k_R')_4$ is subject to “double subtraction errors” is in our view not worthwhile pursuing since an exact method of data evaluation is in any event available. The fact that this procedure recovers the “exact” values of the heat transfer coefficient should not be surprising. It is well known, for example, in the field of chemical kinetics that it is necessary to fit the integrated rate equations to the experimental data rather than to carry out mass balances at a given point. This argument applies especially to the differential equation which includes the heater calibration pulse which is clearly more non-linear as well as more inhomogeneous than the differential equation that does not contain the heater calibration pulse.

We have found also that determination of a heat transfer coefficient $(k_R')_6$ based on the application of the non-linear regression procedure to θ -t profiles in the absence of the calibration pulse, ΔQ , ie where the only perturbation of the system is due to the addition of the solvent gives values that are close to $(k_R')_5$; this is to be expected. For instance, it is well known in the field of relaxation techniques that any perturbation of the system is sufficient for the determination of kinetic data. It follows that it is advantageous in this form of calorimetry to allow the cell contents to change with time as the θ perturbation due to the make-up of the cell suffices for the determination of all the required parameters.

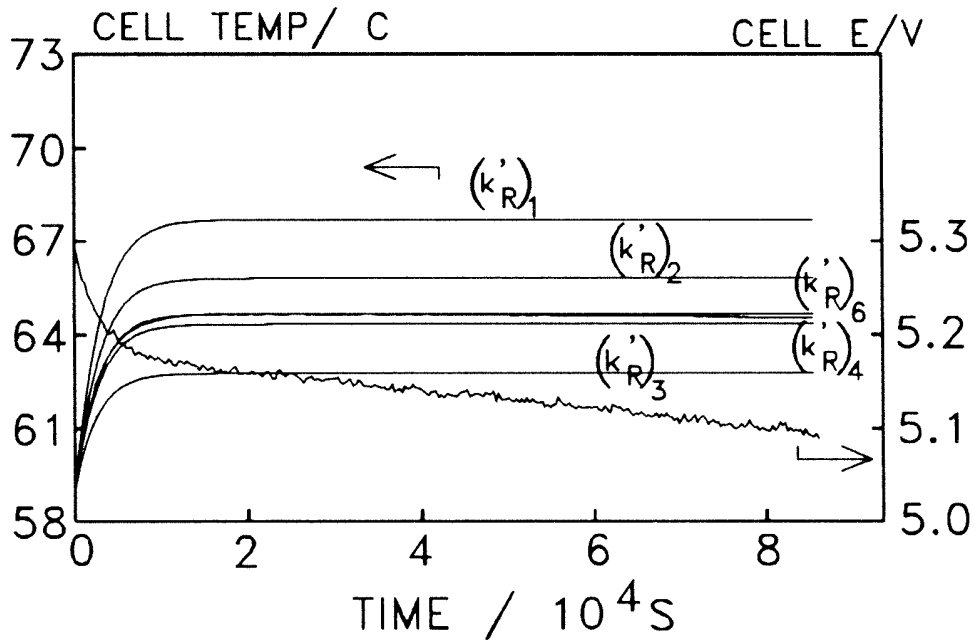


Fig. 5. Simulations of the cell response using the various heat transfer coefficients for a three parameter model.

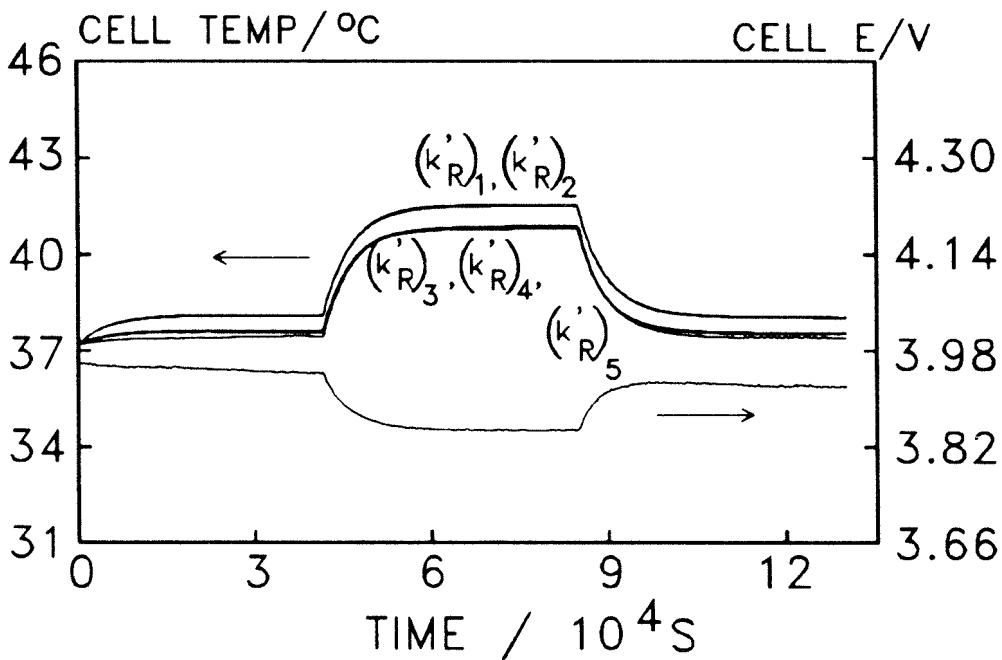


Fig. 6. Simulations of the cell response for a four parameter model.

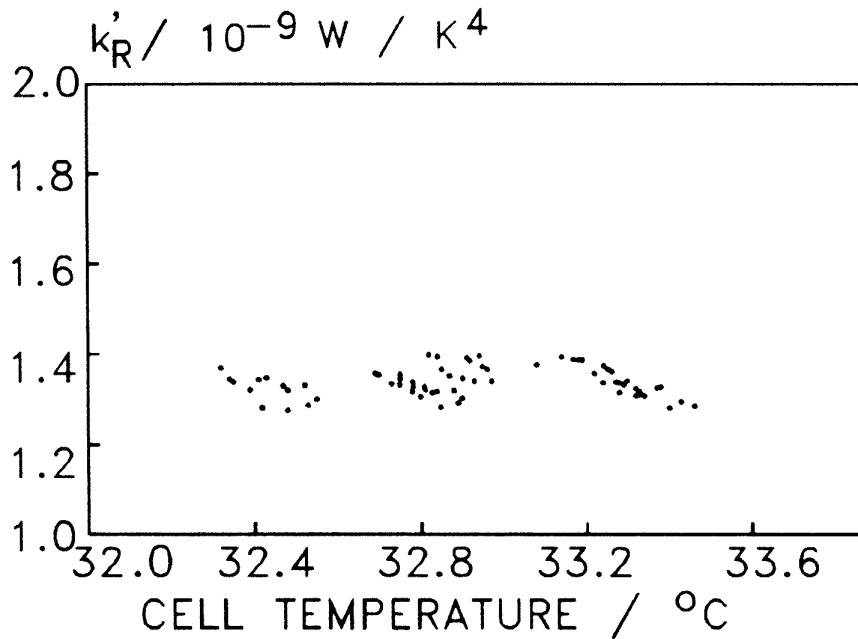


Fig. 7. Plot of the heat transfer coefficients as a function of the cell temperature.

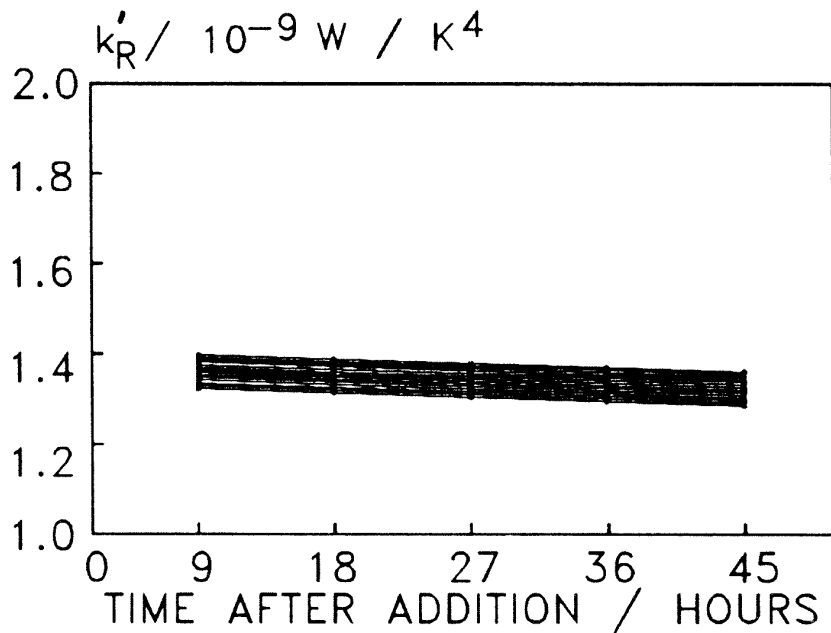


Fig. 8. As Fig. 7 except plotted as a function of the time of determination after cell filled.

We note here also that the heat transfer coefficients $(k'_R)_1 - (k'_R)_6$ are apparent values in that any contribution due to conduction through the top of the cell is included in the radiation term (see above). The use of such apparent radiative heat transfer coefficients leads to an underestimate of the heat output from the cell.⁽⁴⁾ Coefficients derived according to the procedures

embodied in equations (1) – (4) invariably show considerable scatter eg Fig. 7. This scatter is entirely due to systematic errors induced by uncertainty in the level of filling of the cells since sequences of measurements fall on parallel straight lines, Fig. 8. Indeed superposition of the results at the center point shows that the residual error is given by 0.155%. However, in view of the uncertainty of the values of M^0 at any given time, the heat balances can only be derived following a calibration of the cell and, as has been noted above, a non-linear regression procedure should be used to evaluate the three or four parameters governing the behavior of the “black box” model. Since up to 1000 measurement points are used in each evaluation, a very high level of accuracy can be achieved, this accuracy being set mainly by the precision of our measurement of the power inputs to the resistive heaters.

Moving on Towards Clearer Demonstrations of Excess Enthalpy Generation

The careful analyses of the behavior of the calorimeters described have provided us with a reliable, accurate testing system for determination of enthalpy generation and heat flows for electrochemical experiments. We have been interested more recently in systems that lead to conditions which deviate markedly from the relatively low levels of excess enthalpy generation such as that shown in Figs. 9 and 10. In these systems, the cell contents are driven to boiling under conditions where the excess enthalpy generation is far greater than the total enthalpy input. Under these conditions, it is found that the heat transfer is almost totally dominated by evaporation of the cell contents through the vents in the top of the cell, and the need to determine a heat transfer coefficient due to conduction or radiation becomes somewhat academic.

Application of our models to sections of the data of cells containing blank electrode/electrolyte combinations (D_2O solutions with Pt cathodes or H_2O solutions with Pd cathodes) gives $Q_f \approx 0$ indicating the adequacy of the modelling procedures that we have adopted as well as the applicability of this type of calorimetry to the study of electrode reactions. It is of interest that, as expected, the use of $(k_R')_1$ and $(k_R')_2$ in the analysis of these blank cells indicates endothermic operation (which is clearly impossible) whereas the use of $(k_R')_3$ indicates exothermic operation (which is highly unlikely). Only the use of $(k_R')_5$ or $(k_R')_6$ indicates thermal balance. It is also of interest that this thermal balance is maintained even when the cell current is raised so as to drive the cell towards the boiling point. A more demanding test of the calorimetry is based on the cumulative production of excess enthalpy: no cumulative excess enthalpy is predicted during the entire course of the experiment. The exact balance using the best estimate of k_R' indicates the adequacy of the modelling and evaluation procedures. We note also that we can obtain an exact material balance by accounting for electrolysis and evaporation even when the cell is driven to high temperatures.

Application of the same procedures to cells containing palladium based cathodes in D_2O electrolytes, however, show excess enthalpy generation for all cells tested when analyzed by the

same procedures. Of more interest is the fact that the cell contents themselves are evaporated from the cell at a rate that cannot be explained by consideration of the values of the total enthalpy input, even if the heat transfer coefficient is considered to be zero. It is clear that near the boiling point, as mentioned above, the heat flow is totally dominated by evaporation from the cell and that it is impossible to explain the evaporation of the entire contents of the cell in the time scales observed by Joule heating. Fig. 11 shows one example of such behavior (the rate of excess energy generation required to explain the evaporation is ≈ 50 watts corresponding to specific excess of ≈ 1200 watts cm^{-3}).

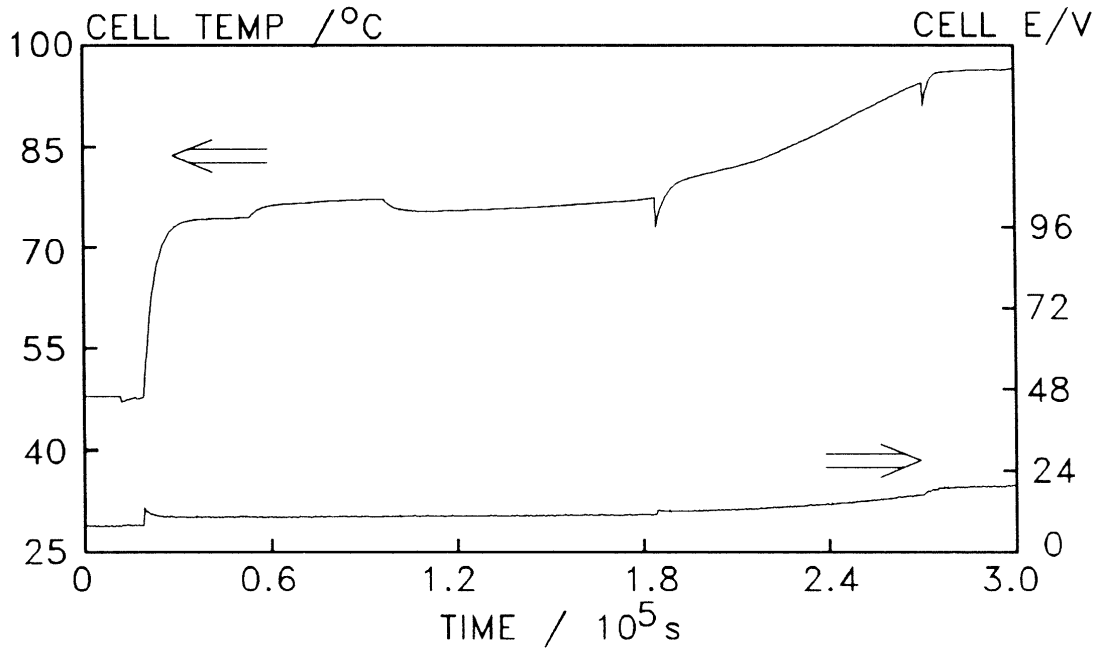


Fig. 9. Typical cell response for a cell which drives itself to boiling.

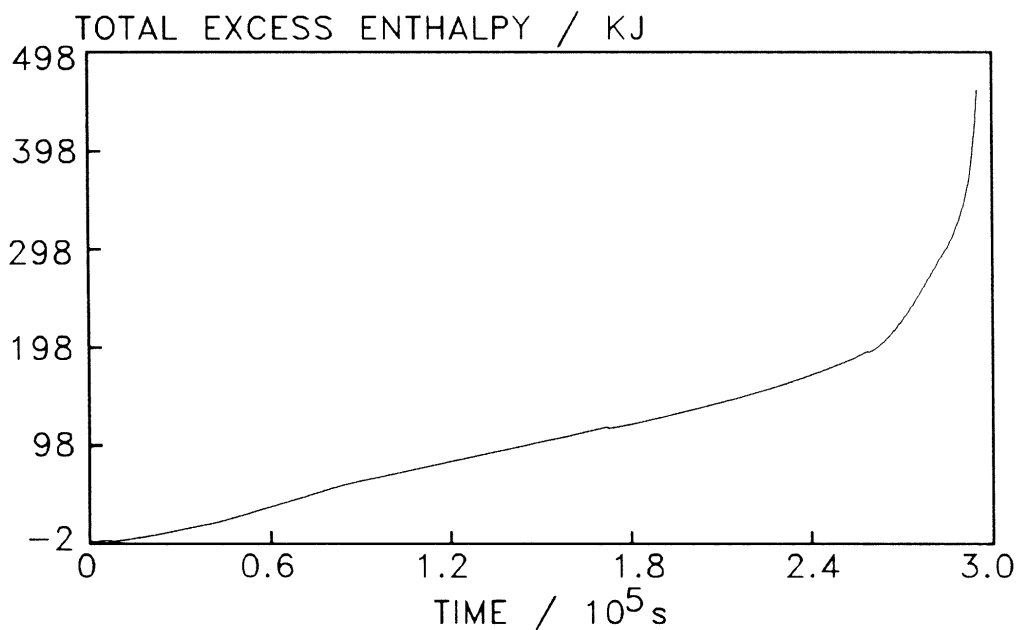


Fig. 10. Plot of the accumulated excess enthalpy for the cell in Fig. 9.

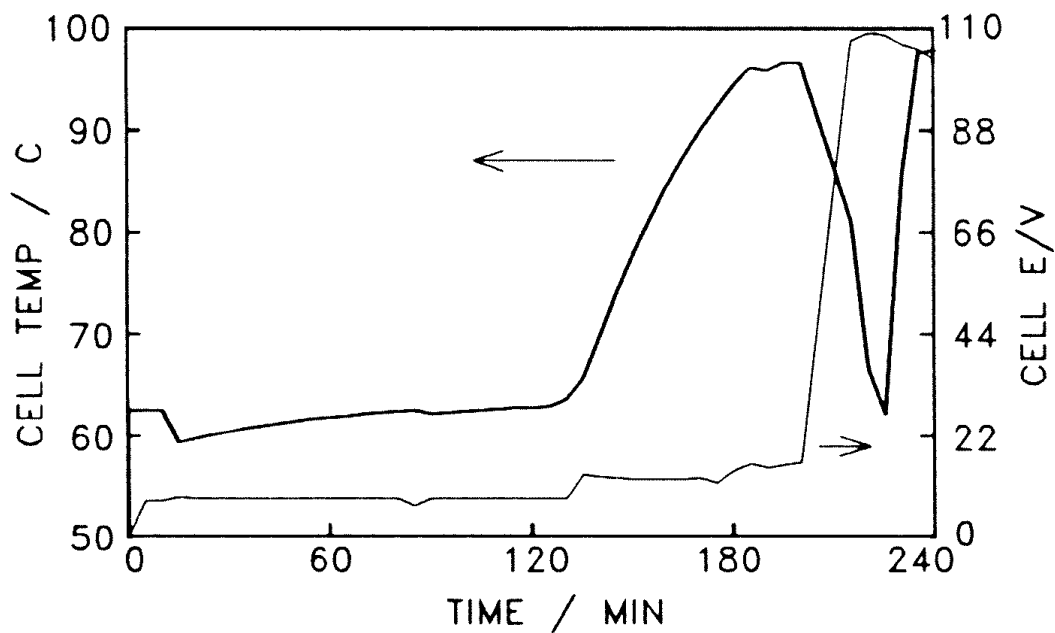


Fig. 11. Cell response for a system which boils out the total cell contents in a short period of time.

While these systems are intriguing, we note here that under such conditions, these calorimeters are very energy inefficient sources of heat, and the next generation of calorimeters must be designed to take this fact into consideration.

Finally, our most recent work is directed toward the design of new sealed calorimeter systems which are not complicated by the factors introduced by applying external power input. Such devices are based entirely on attaining the necessary critical operating conditions in the cathode lattice using new types of enhancement. These conditions are the same that we have previously described, except that these new devices are, in essence, “self-driven” to the extent that the observed excess enthalpy generation is continuous and initiated completely within the device. The observed excess enthalpies are at least 5 orders of magnitude larger than the magnitude of any possible driving forces inside the device. Thermal measurements are then reduced to the trivial measurement of absolute temperatures of operating and blank cells.

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