

More about Positive Feedback; more about Boiling

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Introduction

We have already described elsewhere (1,2) some of the principles which have guided our search for the generation of high rates of excess enthalpy generation at elevated temperatures, say, up to the boiling points of the electrolytes (3,4). One of these principles has been the prediction that the partial molar enthalpy of absorption of hydrogen (or deuterium) in palladium (5) will become positive at the high charging ratios ($X = D/Pd$) required for excess enthalpy generation (6,7), see Fig 1.

Although a transition from exothermic to endothermic absorption is probably not a necessary condition for achieving excess enthalpy generation at elevated temperatures¹, such a transition will certainly facilitate the achievement of high charging ratios. For example, increases of temperature will then themselves lead to increases in X and thereby in the rates of excess enthalpy generation. These are the conditions required for the development of “positive feedback” and, in this paper, we report on two lines of investigation which have indicated the presence of these effects². We then outline the way in which our understanding of this phenomenon has guided our investigation of excess enthalpy generation at elevated temperatures.

“Positive Feedback”

The most direct and systematic evidence for the presence of “positive feedback” can be obtained from the routine calibrations at long experiment times of the Pd/D₂O system in the isoperibolic calorimeters which we use in parts of our investigations (for an illustration see Fig 4A (8)). As we have described elsewhere (1,2,3,4), we have laid considerable stress on the “lower bound heat transfer coefficient (k_R')₁₁”, obtained from the experimental data by assuming that there is no source of excess enthalpy in the cell, $Q_f(t) = 0$. Rearrangement of the differential equation governing the behaviour of the cell gives

¹Thus the application of a sufficiently large difference in Galvani potential (either between a Pd-cathode and the electrolyte or within the metal phase itself) will always be able to counteract the effects of the heat of absorption if this remains exothermic.

²We obtained the first evidence for the presence of “positive feedback” during 1986, a phenomenon which we later described under the euphemistic heading “uncontrolled releases of thermal energy”. Our subsequent work has been carried out under narrowly and tightly controlled conditions to limit the consequences of these effects.

$$(k'_R)_{11} = \frac{\left[\begin{array}{l} [E_{cell}(t) - E_{thermoneutral,bath}] I \\ + \Delta QH(t-t_1) - \Delta QH(t-t_2) \\ - \frac{3I}{4F} \left[\frac{P(t)}{P^* - P(t)} \right] [(C_{P,D_2O,g} - C_{P,D_2O,\ell}) \Delta \theta(t) + L_{D_2O}] \\ - C_{P,D_2O,\ell} M^0 \frac{d\Delta \theta}{dt} \end{array} \right]}{\left[(\theta_{bath} + \Delta \theta(t))^4 - \theta_{bath}^4 \right]} \quad (1)$$

Here we have assumed that any small conductive contribution to heat transfer, $k_c \Delta \theta$, can be lumped into the radiative term by increasing the true radiative heat transfer coefficient from k_R to k'_R . The reason why $(k'_R)_{11}$ is a lower bound is because the inclusion of any excess enthalpy term must inevitably increase the derived heat transfer coefficient. $(k'_R)_{11}$ can be evaluated at any point of the coupled temperature-time and cell potential-time series, such as the points t_1 , just before the application of the heater calibration pulse (with neglect of $\Delta \theta$) or the time t_2 at the completion of this pulse (with inclusion of $\Delta \theta$): see the schematic Fig 2.

For appropriate blank experiments (Pt in H_2O or D_2O), $(k'_R)_{11}$ rapidly approaches a constant value and the standard deviation of these values is 0.1-0.2% of the mean (see also Fig 4B below). We regard this standard deviation as a measure of the precision of the experiments. The reason why it cannot be regarded as a measure of the accuracy (even for blank experiments) is because the possible reduction of electrogenerated oxygen would contribute an extra rate of enthalpy generation (electrogenerated hydrogen or deuterium cannot be re-oxidised at oxide-coated Pt anodes). It is necessary, therefore, to calibrate the system so as to compare the precision of $(k'_R)_{11}$ with the accuracy of (k'_R) . The simplest way of achieving such calibrations is to make a thermal balance at a single point in time, just before the termination of the calibration pulse, $t = t_2$, Fig 2. We have designated the heat transfer coefficient derived in this way as $(k'_R)_2$:

$$(k'_R)_2 = \frac{\left\{ \begin{array}{l} [E_{cell}(\Delta \theta_1, t_2) - E_{cell}(\Delta \theta_2, t_2)] I + \Delta Q \\ - \frac{3I}{4F} \left[\frac{P(\Delta \theta_2, t_2)}{P^* - P(\Delta \theta_2, t_2)} \right] [(C_{P,D_2O,g} - C_{P,D_2O,\ell})(\Delta \theta_2)_{t_2} + L_{D_2O}] \\ + \frac{3I}{4F} \left[\frac{P(\Delta \theta_1, t_2)}{P^* - P(\Delta \theta_1, t_2)} \right] [(C_{P,D_2O,g} - C_{P,D_2O,\ell})(\Delta \theta_1)_{t_2} + L_{D_2O}] \\ - C_{P,D_2O,\ell} M^0 \left(\frac{d\Delta \theta}{dt} \right)_{\Delta \theta_2, t_2} + C_{P,D_2O,\ell} M^0 \left(\frac{d\Delta \theta}{dt} \right)_{\Delta \theta_1, t_2} \end{array} \right\}}{\left[(\theta_{bath} + (\Delta \theta_2)_{t_2})^4 - (\theta_{bath} + (\Delta \theta_1)_{t_2})^4 \right]} \quad (2)$$

The relative standard deviations of $(k'_R)_2$ are in the range 1-2% of the mean and these standard deviations are measures of the accuracy which can be achieved by

making thermal balances at a single point in time. The principal reason for the order of magnitude difference between the precision of $(k_R')_{11}$ and the accuracy of $(k_R')_2$ is the fact that the denominator of (2) is determined by the difference of two comparably large terms, whereas that of (1) is determined by one of the terms alone³.

For the investigation of blank experiments (Pt in H₂O or D₂O), we find that the heat transfer coefficients related to $(k_R')_{11}$ are somewhat smaller than those related to $(k_R')_2$ (we describe these heat transfer coefficients with the generic designations $(k_R')_{i,1}$ and $(k_R')_{i,2}$). We believe that the reason for this small difference is the contribution of a small rate of excess enthalpy generation due to the reduction of electrogenerated oxygen, see above (1,2). By contrast to these blank experiments, $(k_R')_{11}$ for the Pd-H₂O system is initially markedly reduced, so much so that under suitable conditions $(k_R')_{11}$ may be negative at short times. The reason for this reduction in $(k_R')_{11}$ is the exothermic dissolution of H in Pd. However, this phenomenon decays with the diffusional relaxation time and at longer times $(k_R')_{11}$ is again closely similar to the true value of the heat transfer coefficient, $(k_R')_2$.

The condition $(k_R')_{11} < (k_R')_2$ is maintained for prolonged periods of time, typically 2-6 weeks. However, at sufficiently long times we frequently observe a strange reversal of behaviour in that $(k_R')_2$ apparently becomes smaller than $(k_R')_{11}$. Such behaviour must have a quite special explanation because the condition $(k_R')_2 < (k_R')_{11}$ is forbidden by the Second Law of Thermodynamics (taken at its face value, the cell would have to behave as a spontaneous refrigerator to explain the result). The condition $(k_R')_2 < (k_R')_{11}$ is maintained for a limited period of time but eventually the system reverts to the expected behaviour, $(k_R')_{11} < (k_R')_2$.

We illustrate this transition with three calibration cycles taken from the results accumulated under the Japanese New Hydrogen Energy Project⁴, Figs 3A-C. It will be seen that the transition is associated with further peculiarities. The temperature-time series both before and after the transition show the expected approach to a quasi-steady-state following the application of the heater calibration pulse and a relaxation to the base line following the termination of this pulse⁵, Figs 3A and C. By contrast, during the transition, Fig 3B, the temperature does not approach a quasi-steady-state at the end of the calibration pulse, nor does the temperature relax to the base line at

³We have described elsewhere (1,2,3,4) changes in the methods of data processing which allow us to increase the precision of $(k_R')_{11}$ and the accuracy of $(k_R')_2$ by factors of $\cong 10$. These methods rely on the use of the integrals of the experimental quantities rather than on evaluations at single points in time as for $(k_R')_{11}$ and $(k_R')_2$. These enhancements of the precision and accuracy are not required for the discussion of the topics considered in the present paper except for the comparison outlined in the following paragraph.

⁴We are greatly indebted to NHE for permission to use this illustration, as well as that in Fig 4A.

⁵As the temperature-time and cell potential-time series are coupled, see equations (1) and (2), the thermal relaxation times depend on both time series. A rough approximation is (9)

$$\tau = \frac{C_{p, \text{cell}} M^0}{\left[4k_R' \theta_{\text{beh}}^2 - \left(\frac{dE_{\text{cell}}}{d\Delta\theta} \right) I \right]} \quad (3)$$

A more exact result based on a series-type solution of the differential equation governing the behaviour of the calorimeters is available as an internal Technova Report. As $(dE_{\text{cell}}/d\Delta\theta)$ is negative (see Figs 3A-C), the temperature dependence of E_{cell} shortens τ from the external value. Indeed, the two terms in the denominator of (3) are of comparable magnitudes and we expect that the cells should show “negative feedback” under normal conditions.

the end of this pulse (compare the behaviour of the cells investigated by the group at Harwell, Figs 2A and B (8)). We have to conclude that the temperature rise induced by the heater calibration pulse itself induces an increase in the rate of generation excess enthalpy both during the application of the calibration pulse as well as after its termination. These are the conditions required for “positive feedback” which is evidently sufficiently marked to outweigh the normal “negative feedback” shown by the cells.

It is a consequence of the “positive feedback” that the temperature at the end of the calibration pulse is higher than it would be in the absence of such feedback. As a result, $(k_R)_2$ is smaller than expected so that we can reach the condition $(k_R)_2 < (k_R)_{11}$.

A possible explanation of the onset of “positive feedback” is a reversal in the heat of absorption at sufficiently high charging ratios, Fig 1. Although other explanations could be invoked (and should be explored), it is natural to search for direct evidence of changes in the heat of absorption - a matter of some difficulty. A possible approach is the detailed examination of the variation of $(k_R)_{11}$ with time in the region of the calibration pulses because transient sources of excess enthalpy in the cell affect $(k_R)_{11}$ directly. Fig 4A shows one such example: we see that the application of the heater pulse leads to a transient increase in $(k_R)_{11}$ which must be interpreted as a transient endothermic process in the cell. We observe this positive excursion in $(k_R)_{11}$, although the longer-term effect of the application of the calibration pulse is a decrease of $(k_R)_{11}$ which must be due to an increase in the rate of excess enthalpy generation. We note also that if the effects of “positive feedback” are not fully established, we would expect to see a transient decrease in $(k_R)_{11}$ at the termination of the heater calibration pulse due to the reversal of endothermic absorption, i.e. the establishment of transient exothermic desorption. Such effects can, indeed, sometimes be observed as in the example shown in Fig 4A.

The behaviour of $(k_R)_{11}$ shown in Fig 4A should be judged in the context of the variability of $(k_R)_{11}$ observed in typical blank experiments, Fig 4B (see also above). In the interpretation of such data it should be borne in mind that about one-third of the standard deviation of the measurements is due to the systematic decrease of $(k_R)_{11}$ with time during any given two-day period⁶.

We note finally that the experiments give other evidence for the presence of a reversal of the heat of absorption. Thus in the region where we observe “positive feedback”, we also observe fluctuations in the cell temperature and cell potential (3,4). These fluctuations may be quite small (as for the Pd-systems) or marked (as, especially, for Pd-Rh alloys), regular or, in the limit, chaotic. We observe that such oscillations would be expected in the region where $\Delta H = 0$ because the fluctuations in entropy will become unbounded. However, it is likely that the reversal in the heat of absorption is itself due to a complex phenomenon such as the formation of the proposed third γ -phase (10). Phase transitions would also lead to oscillatory behaviour.

More about Boiling

The explanation of the effects of “positive feedback” in terms of a reversal of sign of the partial molar enthalpy of absorption with increasing charging ratio, Fig 1,

⁶This period is set by the time interval between the “topping-up” of the cells to make up for losses of D₂O due to electrolysis and, at temperatures approaching the boiling point, due to evaporation.

also provides us with a rationale for other features of the behaviour of the Pd-D₂O system. Thus, it is likely that the achievement of pronounced levels of the rates of excess enthalpy generation requires the attainment of the regime of “positive feedback”, which in turn requires the use of prolonged periods of polarisation, a matter to which attention has been drawn repeatedly. However, the attainment of the condition of “positive feedback” is not sufficient to ensure sustained, high, levels of the rates of excess enthalpy generation. Maintenance of the systems in the region giving pronounced oscillations will eventually diminish or even destroy excess enthalpy generation. The explanation of “positive feedback” in terms of the reversal of the sign of the partial molar enthalpy of absorption indicates that the attainment of this regime needs to be coupled to sustained increases in temperature to ensure that the charging ratio will show the necessary increases required to achieve increases in the rates of excess enthalpy generation. It follows that the use of essentially isothermal calorimetry (a strategy which has been followed in most investigations) is ill-advised, indeed self-defeating.

It is desirable therefore to examine the extent to which the reported achievement of boiling conditions (1,2) fits into this overall pattern. The routine calibration of the cells, Figs 5A and B, allows us to monitor the system behaviour and it is certainly true that the rapid increases in temperature towards the boiling point are only achieved following the detection of “positive feedback”, as has been indicated in Fig 3B. The rates of excess enthalpy generation can become very high under these conditions, so much so that the cells are “driven to dryness” in relatively short periods of time (the last half of the cell contents (45 ml) may be evaporated in 11-15 min). The particular cells used (see Fig 4A (8)) are not suitable for accurate measurements and we therefore adopt conservative approaches to the interpretation of the experimental data (1,2). The simplest first step is to calculate the amount of energy available for evaporation of D₂O, Fig 6. Here we have used the true value of the heat transfer coefficient to calculate the radiative output. The total energy available is $\cong 70.5$ kJ, sufficient to evaporate $\cong 1.7$ M of D₂O. This leaves a deficit of 127 kJ required for the evaporation of the remaining 3.05 M D₂O.

In the absence of excess enthalpy generation, we reach a further impossible conclusion. As Fig 6 shows, the cumulative energy would then need to be negative for the first $\cong 7.7$ hours of operation of the cell during the last period of operation. This again contravenes the Second Law of Thermodynamics. We conclude, therefore, that we must necessarily invoke excess enthalpy generation to explain the thermal balancing of the cell. However, our explanation of the behaviour must also be extended to give an account of the time dependence of the cell contents. The simplest assumption which we can make is that which has been used as a basis of the construction of Fig 6. This gives us curve A on Fig 7 and is clearly inadmissible. An alternative assumption is that the total cell contents in D₂O (5 M) are evaporated during the last period of operation, i.e. we rule out that the cell has been driven to boiling (1,2). We can derive such a “force fit” by regarding the atmospheric pressure, P*, as an adjustable parameter. We obtain curve C in Fig 7 and need to postulate the variation of the rate of excess enthalpy generation with time shown in Fig 8. However, such an explanation is again in conflict with other aspects of the experimental evidence. In the first place, we need to assume a value of P* which is below that of the recorded atmospheric pressure. Secondly, we conclude that the cell would then have to have been half-empty some 2.5 hours before achieving “boiling to dryness”,

whereas video recordings show that this point was reached some 11 minutes before “boiling to dryness”⁷. The third assumption which we can make is that the rate of excess enthalpy generation can be calculated using the actual atmospheric pressure. This gives us the lower curve in Fig 8 for the rate of excess enthalpy generation in Fig 8 and the time course, curve B, for the cell contents in Fig 7. We conclude that we must now assume a period of intense boiling to account for the removal of the last half of the cell contents. This is in line with our visual observations and in turn leads to high final rates of excess enthalpy generation shown in Fig 8. The two plots in Fig 8 give the extrema of the behaviour: the actual behaviour must lie between the two limits but clearly closer to that given by the scenario leading to curve B in Fig 7 than that leading to curve C (1,2).

Conclusion

Prolonged polarization of cells containing Pd-based cathodes leads to “positive feedback”, which can be attributed (at least in part) to a change from exothermic to endothermic absorption with increasing charging ratio. Increase of the cell temperature then leads to marked increases in the rates of excess enthalpy generation and enthalpy generation at the boiling point can be achieved.

References

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⁷Although our use of video recordings to time the cell contents has been criticised, we note that it is hardly possible to confuse 11 minutes with 2.5 hours.

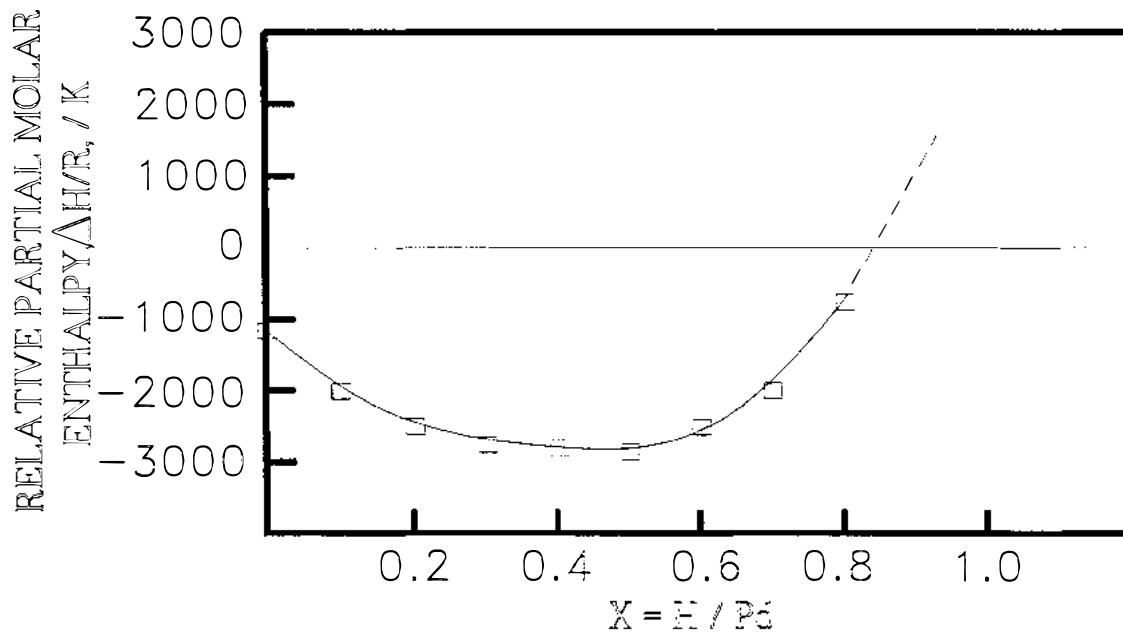


Fig 1. The variation of the relative partial molar enthalpy of hydrogen in palladium as a function of the charging ratio.

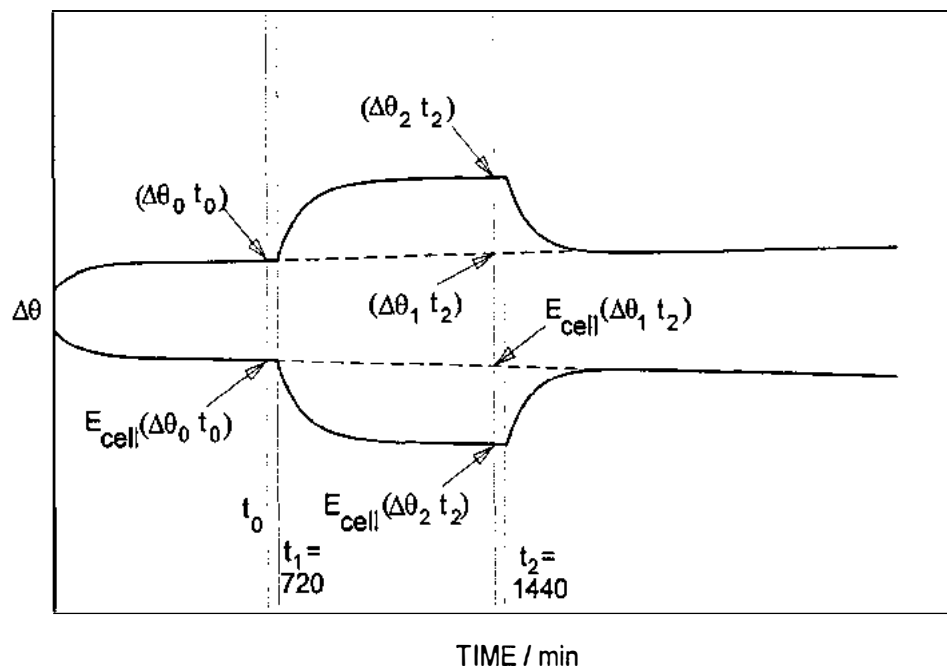


Fig 2. Schematic diagram of the methodology used in the calculations.

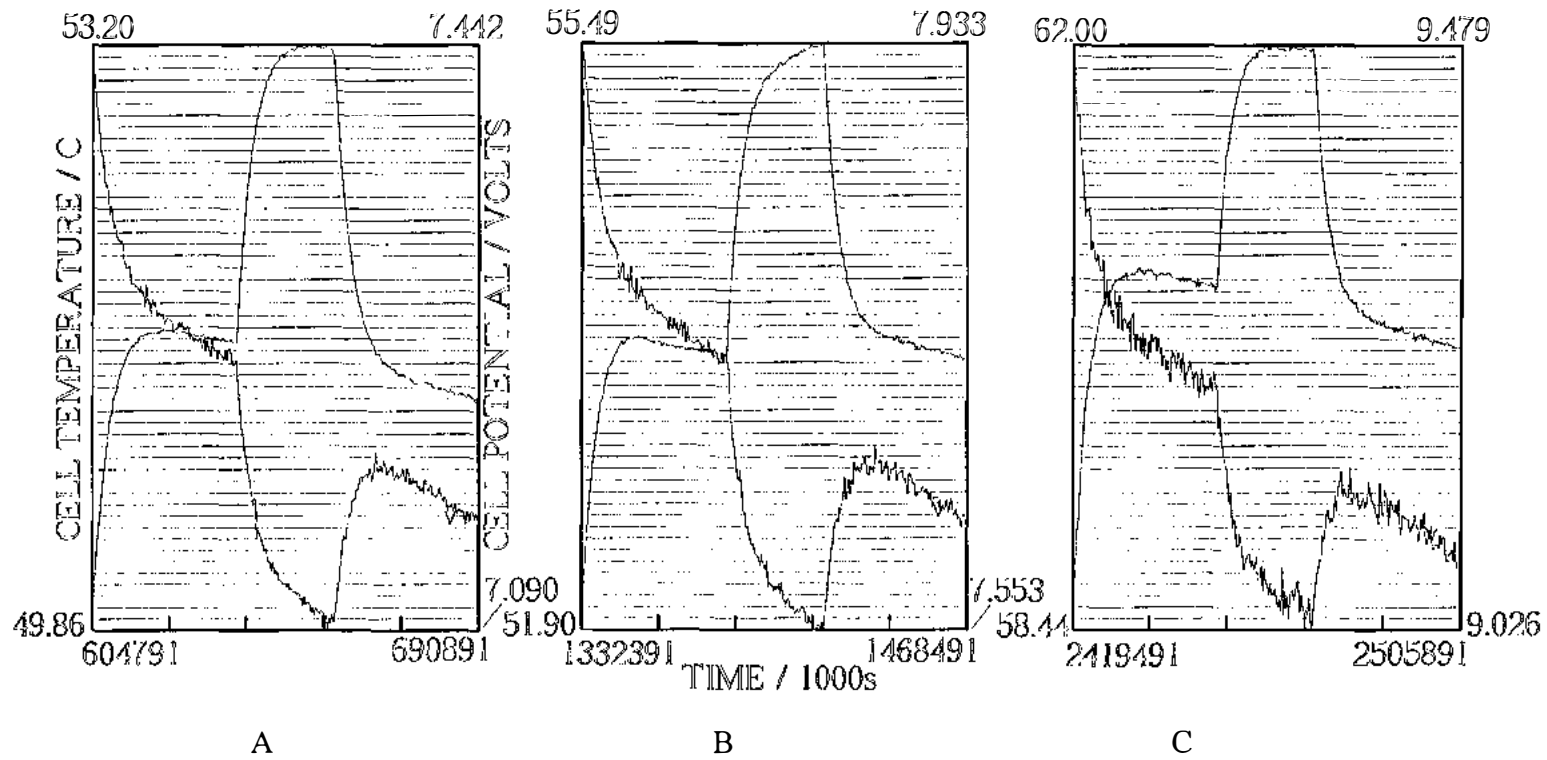


Fig 3. Experiment 4661 of the N.H.E. data sets. Pd 90 Ag10 cathode, 0.4 cm diameter, 1.25 cm length polarized in 0.1 M LiOD in D₂O; cell current = 0.5A, $\Delta Q = 0.2504W$; the "raw data" of the cell temperature and cell potential as a function of time

- A: a calibration before the onset of "positive feedback"
- B: a calibration in the region of "positive feedback"
- C: a calibration after the region of "positive feedback".

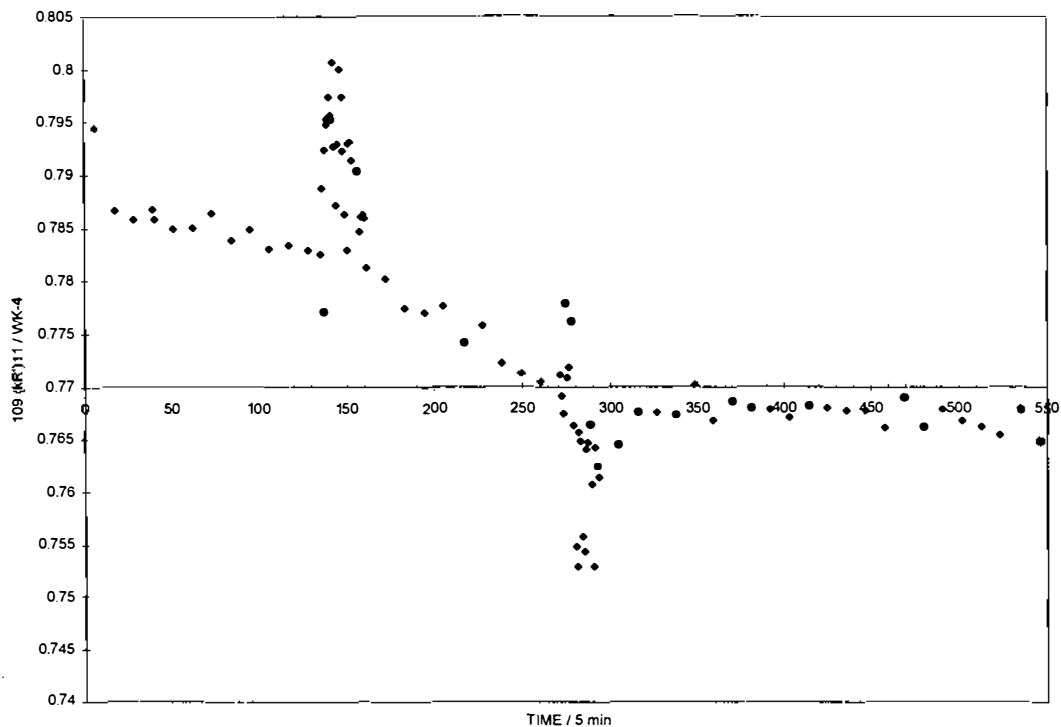


Fig 4A. Experiment 4731 of the N.H.E. data sets. Pd 90 Ag 10 cathode, 0.4 cm diameter, 1.25 cm length polarized in 0.1 M LiOD in D₂O; cell current = 0.2A, $\Delta Q = 0.2504W$; the variation of $(kR')_{11}$ with time during days 33 and 34 of polarization. The start and end of the heater calibration pulse are shown by the positive and negative excursions of $(kR')_{11}$.

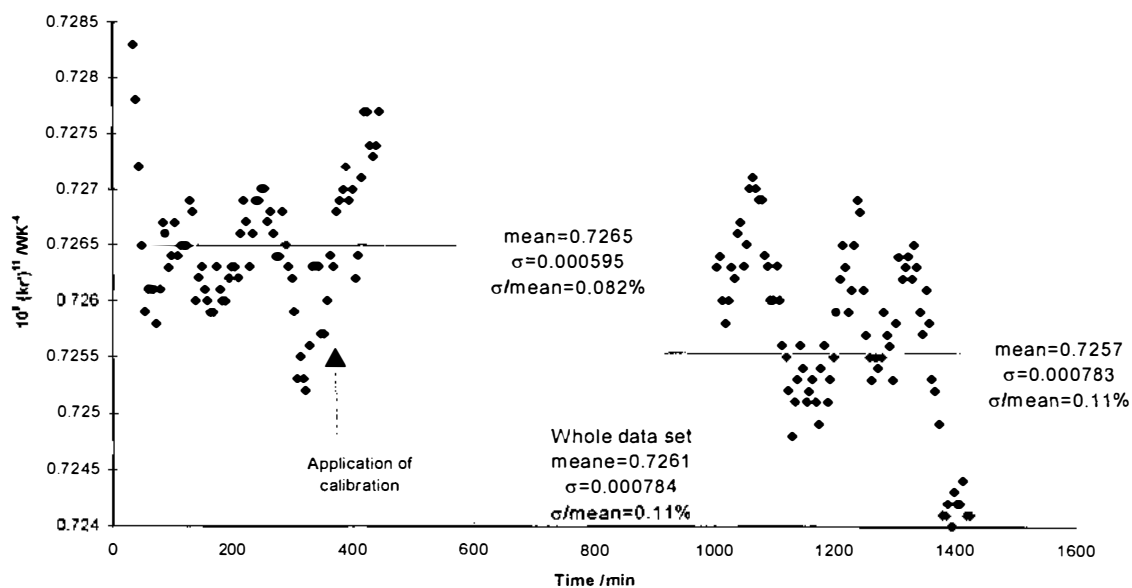


Fig 4B. Variation of $(kR')_{11}$ with time for a blank experiment. Pt cathode 0.125 cm diameter, 1.25 cm length polarized in 0.1 M LiOD in D₂O; cell current = 0.2A. The region before and after completion of the calibration pulse.

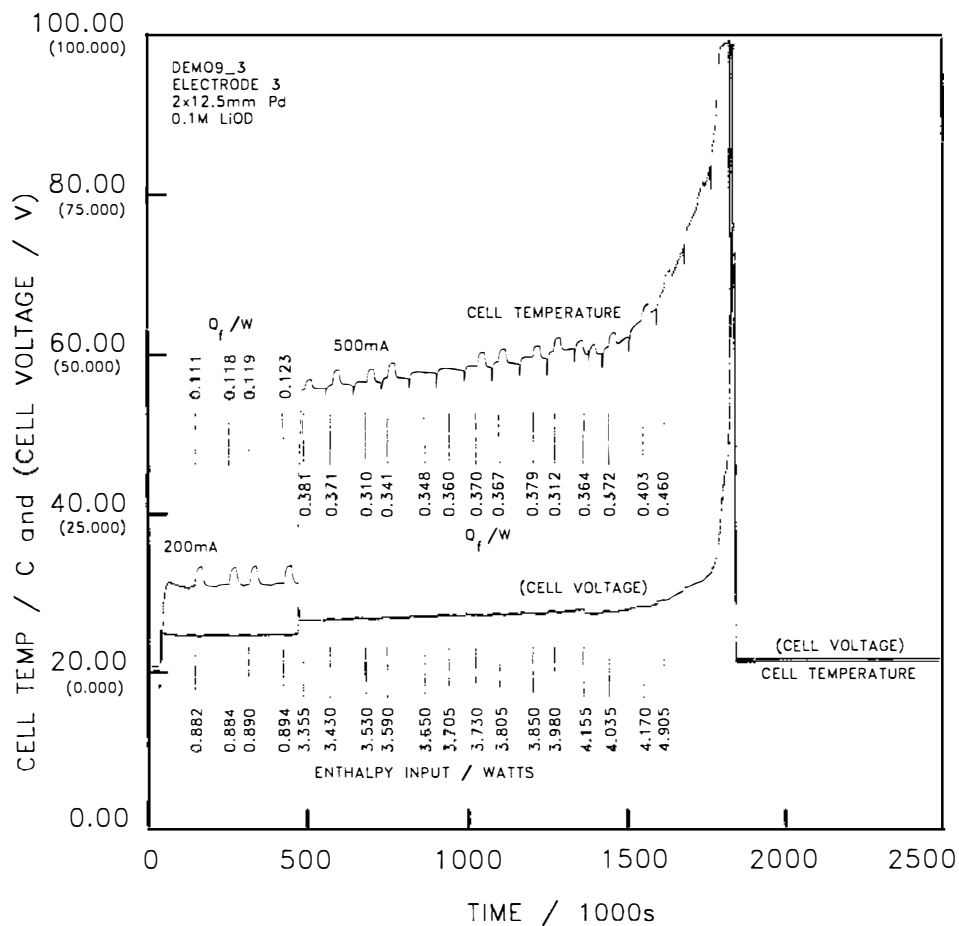


Fig 5A. The cell temperature and cell voltage for a cell driven to boiling. Pd cathode 0.2 cm diameter, 1.25 cm length polarized in 0.1 M LiOD in D₂O; cell current = 0.2A and then 0.5A.

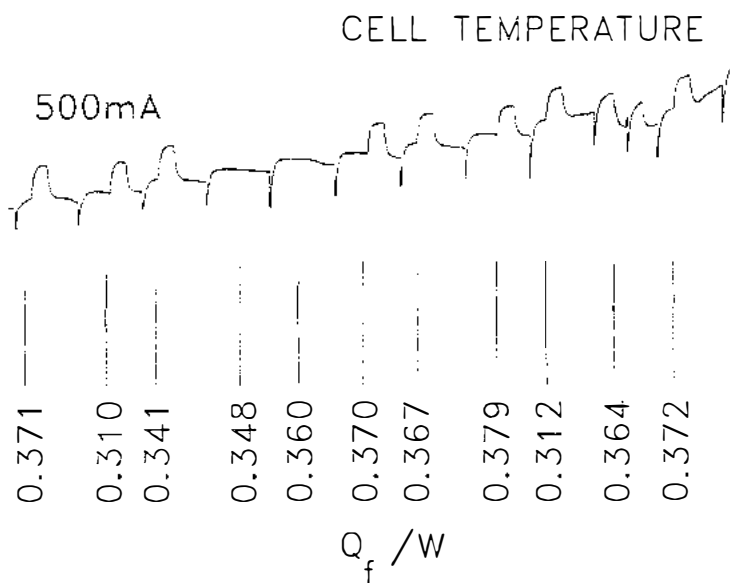


Fig 5B. Enlargement of a section of Fig 5A.

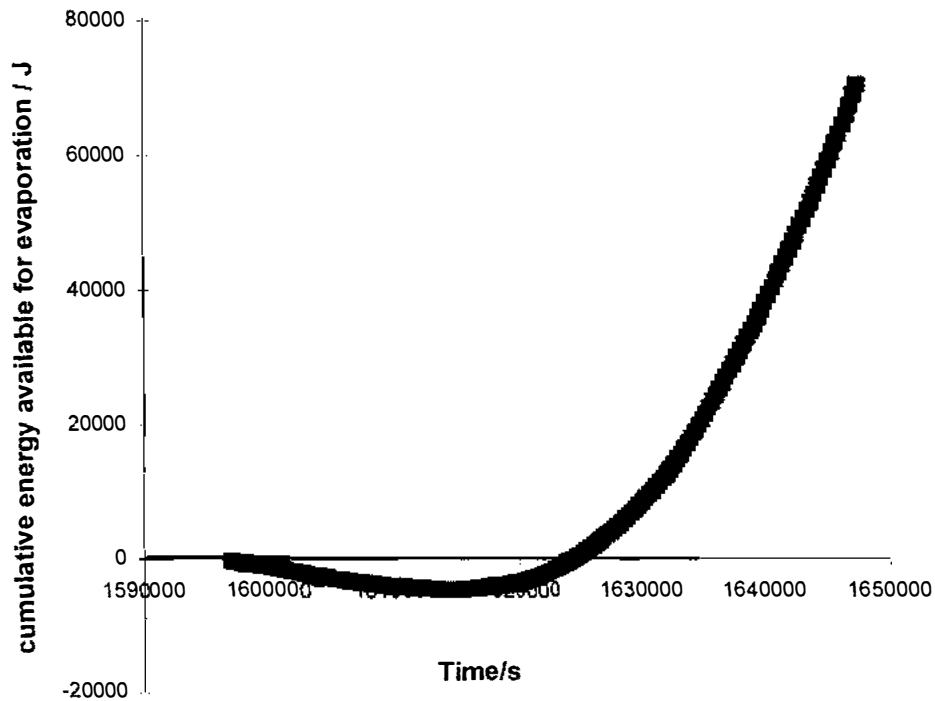


Fig 6. The cumulative energy available for evaporation of D₂O for the last period of operation of the experiment illustrated in Fig. 5A based on the assumption that there is no generation of excess enthalpy.

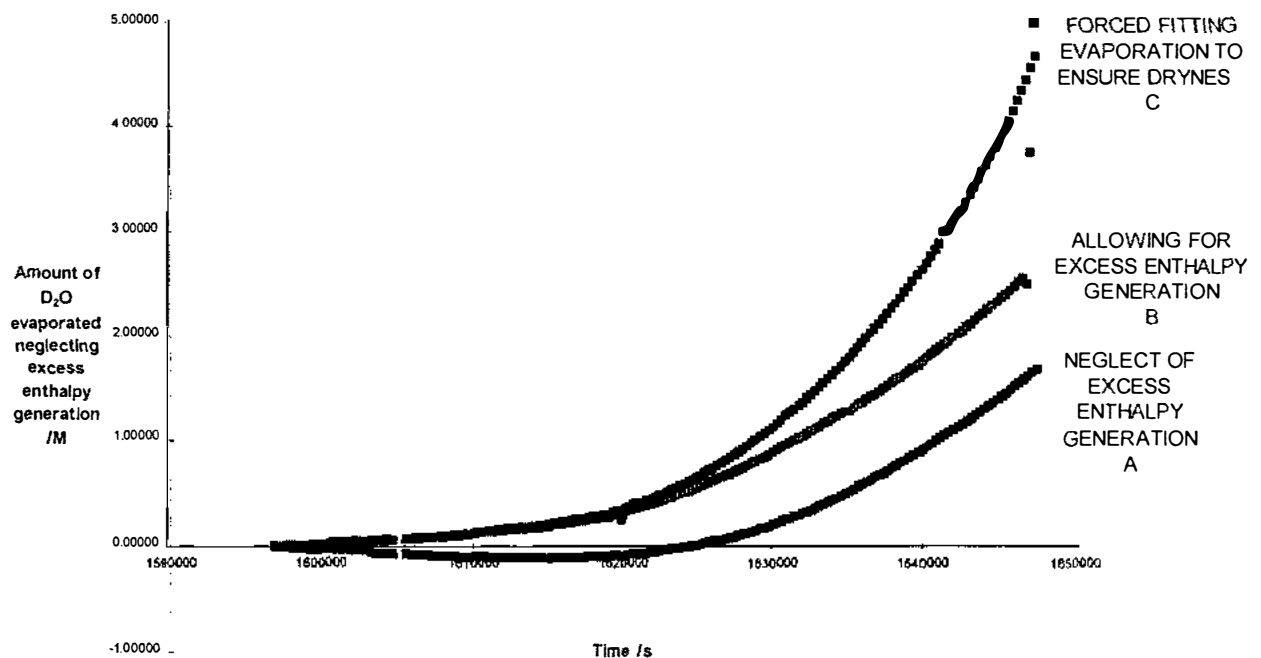


Fig 7. The variation of the evaporated D₂O with time for the last period of operation of the experiment illustrated in Fig 5A.

A: assuming that there is no generation of excess enthalpy

B: including the excess enthalpy calculated from the temperature-time and cell potential-time curves with P* given by the atmospheric pressure

C: as B but with P* reduced to 0.953 bar to force fit the evaporation to be completed during the last period of operation of the experiment.

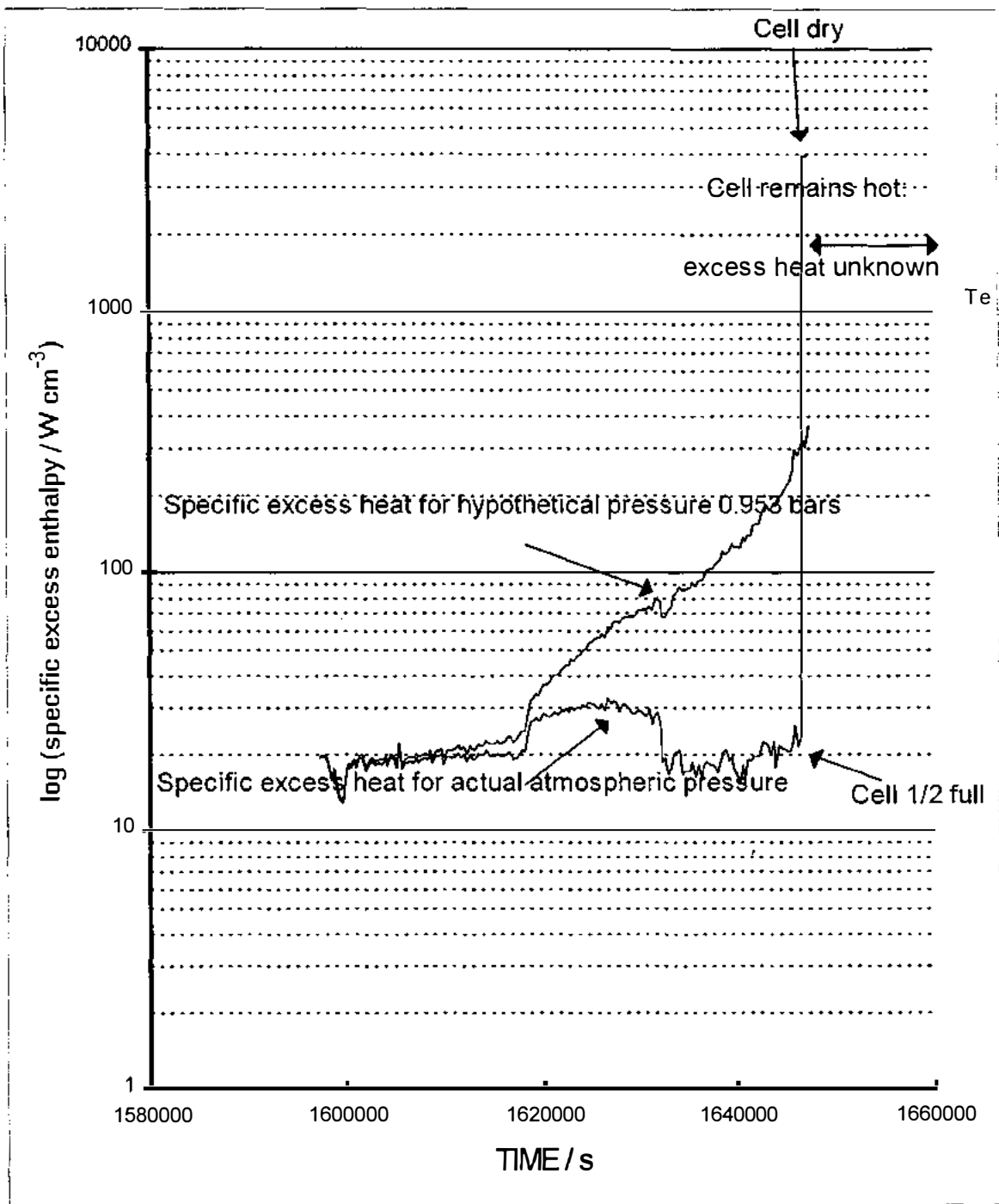


Fig 8. The variation of the rate of excess enthalpy generation with time for the assumptions B and C used in the construction of Fig 7.