

## The Experimenters' Regress

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### Introduction

At the beginning of any new and controversial field of investigation, we cannot tell which of the following two statements is true:

- A. "Positive" conclusions are correct; "negative" results are due to bad experimentation.
- B. "Negative" conclusions are correct; "positive" results are due to bad experimentation.

This is the basis of the Experimenters' Regress, a concept drawn from the field of the Sociology of Science, e.g. see (1). As scientists, we also need to examine the possible validity of the following statement (as well as its corollary):

- C. Key "negative" conclusions have been due to incorrect evaluations/interpretations; the results in fact point to "positive" conclusions.

If statement C applies, then the Experimenters' Regress should be seen to be substantially broken (Sociologists would not agree with this view because their judgements are made in terms of the public perception of fields of study).

Sociologists of Science also express the following view, e.g. see (1):

- D. A discovery is not made at a single point in time.

As Scientists, we might again wish to add some further statements, such as:

- E. Interpretations are not completed at a single point in time.
- F. Interpretations (and calibrations) are affected by our knowledge of the system being studied<sup>1</sup>.

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<sup>1</sup> Unfortunately, the process of data evaluation is frequently curtailed, partly because of the costs involved and partly because of the loss of the "raw data".

We can investigate the applicability of these ideas by considering some of the experimental results obtained by the research group based at Harwell (2) (this has been the key study which has been generally perceived to fall into category B.). Figs 1A and B are sections of experimental temperature-time plots for Cell 3 of the data sets (Cell containing a 6 mm diameter by 1 cm length Pd-cathode polarized at 0.298A in 0.1M NaOD/D<sub>2</sub>O) and for Cell 4 (Cell containing a similar cathode polarized at 0.298A in 0.1M NaOH/H<sub>2</sub>O); see also (3). Figs 2A and B are enlargements of the section containing the application of a heater calibration pulse (denoted by H in Fig 1A). The data for Cells 3 and 4 can be evaluated to give the “lower bound heat transfer coefficients,  $(k_R')_{11}$ ” (4,5,6,7,8) such as those shown in Figs 3A and B. The decrease of  $(k_R')_{11}$  with time shown in Fig 3B is expected because of the progressive falling level of the electrolyte (caused by the electrolysis) in the cell, Fig 4B, used in the Harwell study (these cells were not silvered in their top portions; contrast the cell design, Fig 4A, used in our current studies). We draw attention especially to the fact that superposition of the heater calibration pulse on the Joule heating due to electrolysis does not give any anomalous changes in  $(k_R')_{11}$  indicating correct thermal balancing for this cell (i.e. no generation excess enthalpy). By contrast,  $(k_R')_{11}$  for Cell 3, Fig 4A, does not show the expected decrease with time. We have to interpret this by assuming an overall decrease of a rate of excess enthalpy generation with time (4,5,6,7). However, we also see that the temperature-time curve for Cell 3, Fig 3A, shows one of the tell-tale signatures of “positive feedback” in the region of the heater calibration pulse. The temperature does not relax to the expected baseline following the completion of the calibration; the calibration pulse therefore increases the thermal output (compare (3)). Transient development and loss of “positive feedback” would be expected to lead to “bursts” in the rates of excess enthalpy generation. Evidence for such “bursts” is seen in the temperature-time record for Cell 3, as is shown by comparison of Figs 1A and B.

In view of the presence of these “bursts” as well as of “positive feedback”, Fig 3A, we cannot obtain a valid calibration for Cell 3 from the heater calibration pulse (see especially (8)). For further evaluation of the data, we therefore have to search for special ways of calibrating this cell. One possible approach is to evaluate  $(k_R')_{11}$  at the series of temperature minima, Fig 1A and B, and to use the decrease of  $(k_R')_{11}$  with time determined for Cell 4, Fig 3B, to make estimates of  $(k_R')_{11}$  for Cell 3 at times other than those of the minima. Fig 5B shows that this procedure evidently overestimates the decrease of  $(k_R')_{11}$  with time because the cell becomes progressively endothermic (which contravenes the Second Law of Thermodynamics). Application of the same procedure to Cell 4 must therefore lead to an underestimate of the rate of excess enthalpy generation, Fig 5A. Moreover, this procedure necessarily resets the rate of excess enthalpy generation to zero at each successive minimum, i.e. we cannot detect any underlying progressive changes in these rates.

## Discussion

We can consider the particular section of the results obtained in the Harwell study illustrated in this paper both from the qualitative and the quantitative point of view. As far as the qualitative interpretation is concerned, we observe that it is not

possible to observe increases in the cell temperature, Fig 1 A, without invoking the presence of a source of excess enthalpy. Evidently statement C applies<sup>2</sup>.

In view of the difficulties of achieving calibrations of the cells used in the Harwell study, we can at present achieve at best a semi-quantitative evaluation of the datasets. Such an evaluation shows that the “bursts” in the rates of excess enthalpy generation shown in Fig 5A are of the same order of magnitude as the steady-state rates we observed at comparable current densities in our first studies ( ). In those early studies we also observed prolonged “bursts” in the rates of excess enthalpy generation ( ). One possible reason for the persistence of these “bursts” in the Harwell study is that the electrodes were made of sintered metal of high purity (2). By contrast, the material which we have used in our ongoing programme has been cast from metal of somewhat lower purity. We believe that electrodes made of sintered metal may be especially liable to crack; formation of cracks must lead to deloading of the lattice (10).

We observe that the conclusion that there was no excess enthalpy generation in the Pd/D<sub>2</sub>O system was reached in the Harwell study in the absence of any detailed evaluation of the temperature-time and cell potential-time series, even though the complexities posed by the particular cell design, Fig 4B, were recognised (2). The present and other more detailed investigations of the Harwell data sets (10), however, shows that excess enthalpy generation was in fact observed in that study, contrary to the conclusions reached by the authors (2). Evidently, it is necessary to take into account the statements E and F made above: interpretations of a given set of results are not completed at a single point in time and these interpretations are inevitably affected by our state of knowledge of the systems under study. It is this reinterpretation which leads us to C: the “negative” conclusion reached in the Harwell study was due to incorrect interpretations and the results in fact pointed to “positive” conclusions.

### Acknowledgement

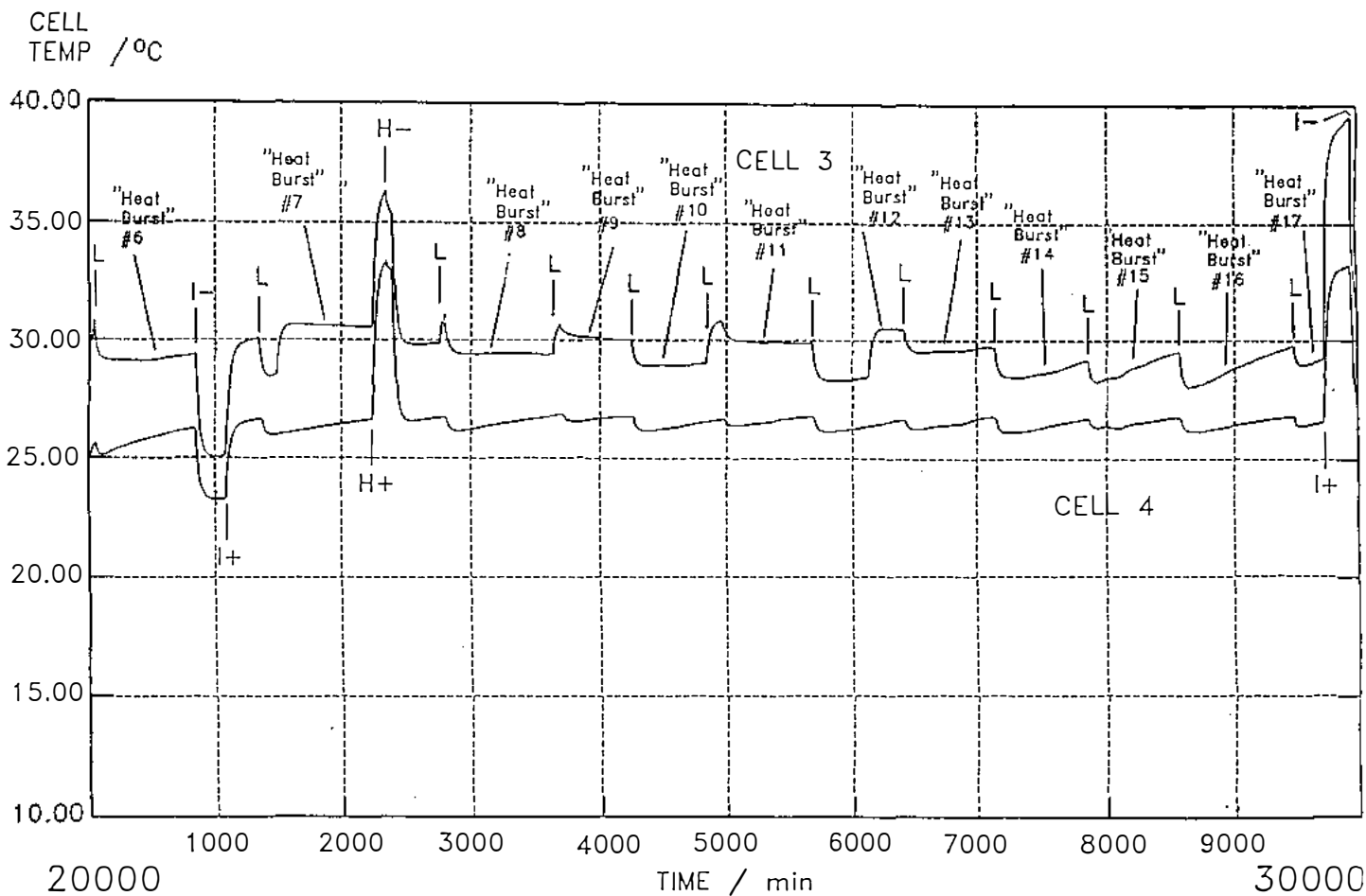
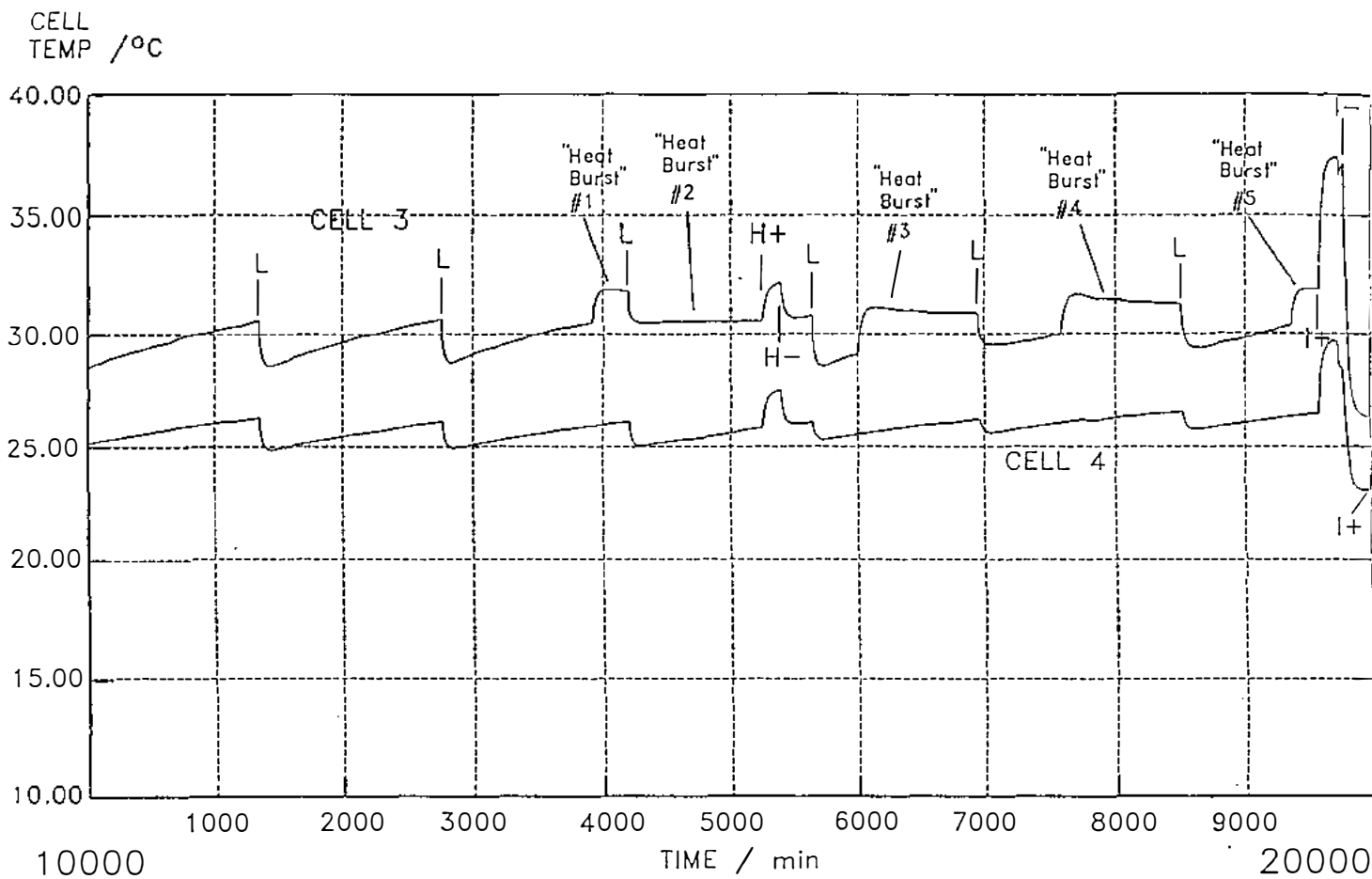
It is greatly to the credit of the research group at Harwell that they have made their “raw data” available for further study.

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<sup>2</sup> The only alternative is to assume that there were malfunctions in the instrumentation. It is not possible to conclude that the instrumentation was operating correctly yet that there was no generation of excess enthalpy, which was the conclusion reached in the Harwell study (2).

## References

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11. to be published.



Figs 1A and B. Sections of the temperature-time plots for Cell 3 (containing a 6 mm diameter by 1cm length Pd-cathode polarized at 0.298A in 0.298A in 0.1M NaOD/D<sub>2</sub>O) and Cell 4 (containing similar cathode polarized in 0.1M NaOH/H<sub>2</sub>O).

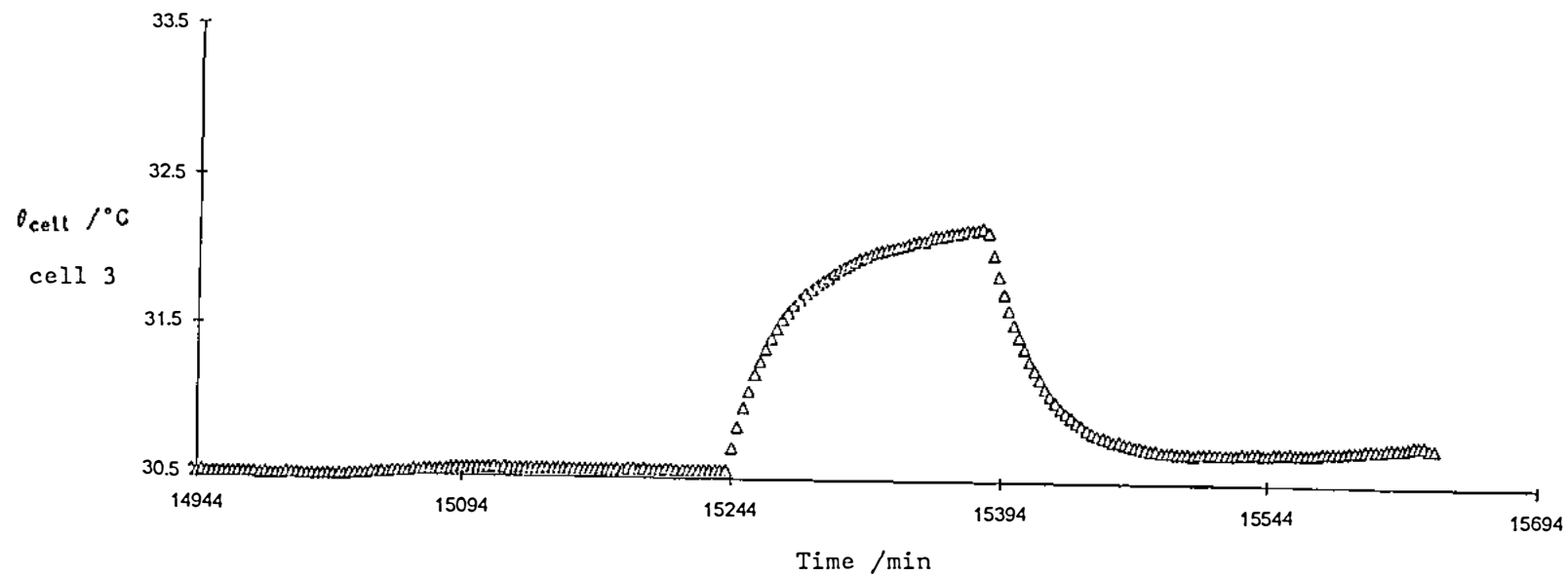


Fig 2A. Enlargement of the section covering the application of an heater calibration pulse to Cell 3 (denoted by H in Fig 1A).

157

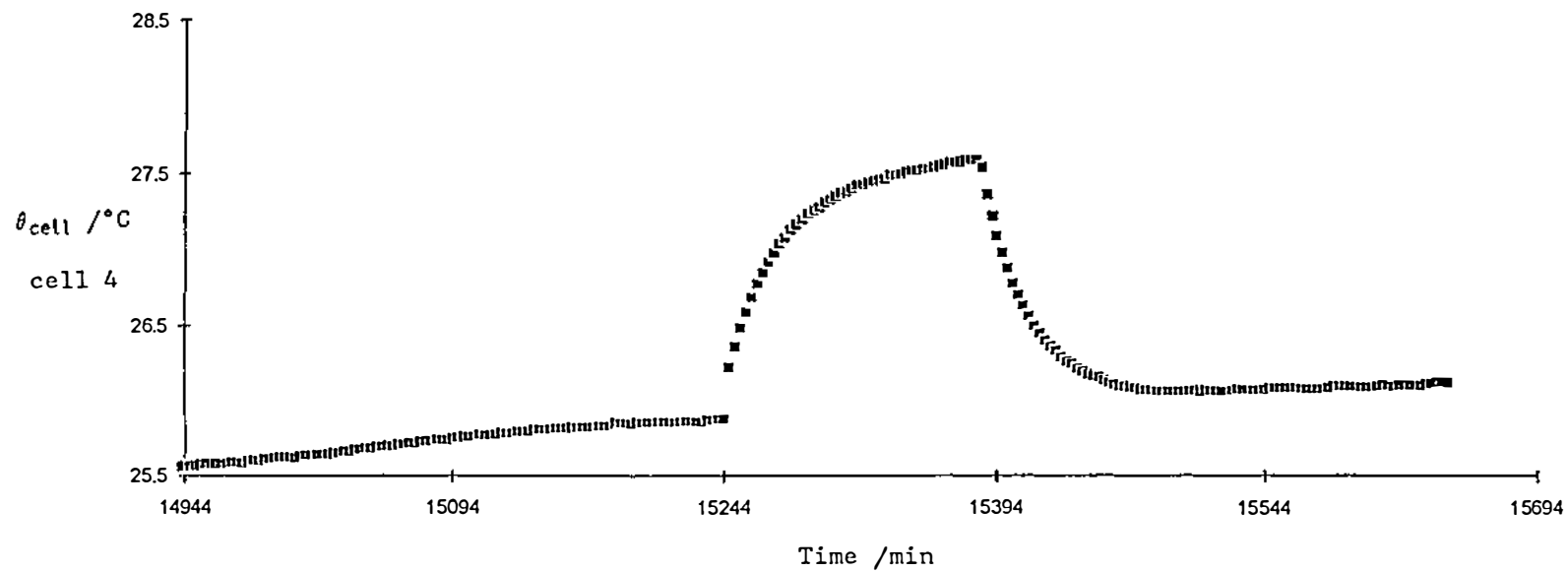


Fig 2B. Enlargement of the section covering the application of an heater calibration pulse to Cell 4 (denoted by H in Fig 1A).

CELL 3

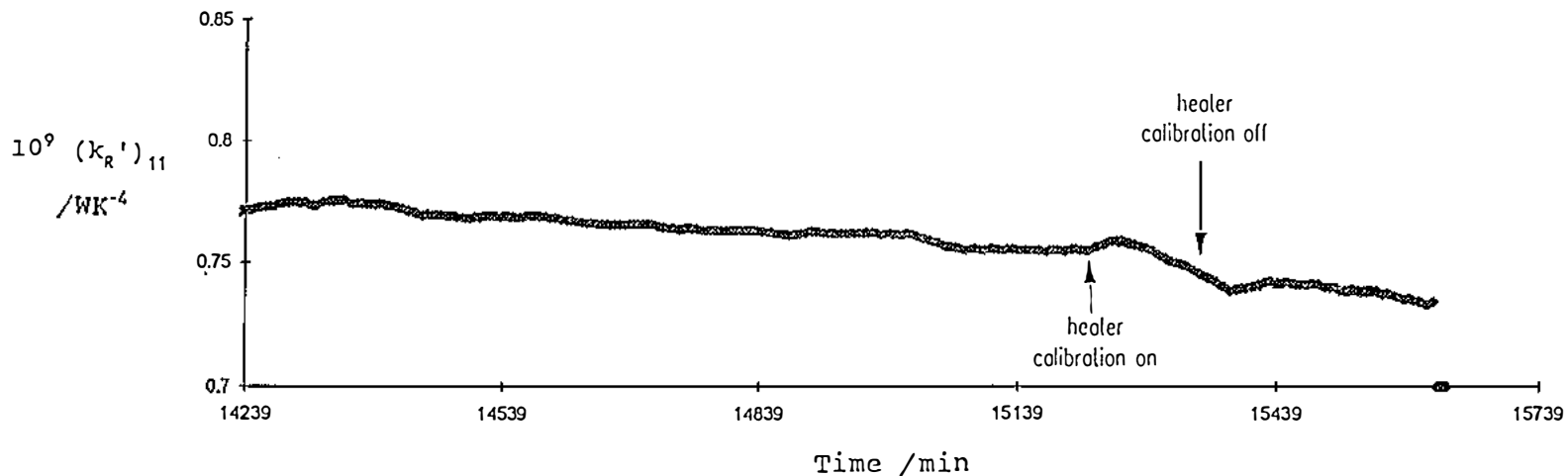


Fig 3A. The lower bound heat transfer coefficient,  $(k_R')_{11}$ , as a function of time for the section of data for Cell 3 illustrated in Fig 2A.

158

CELL 4

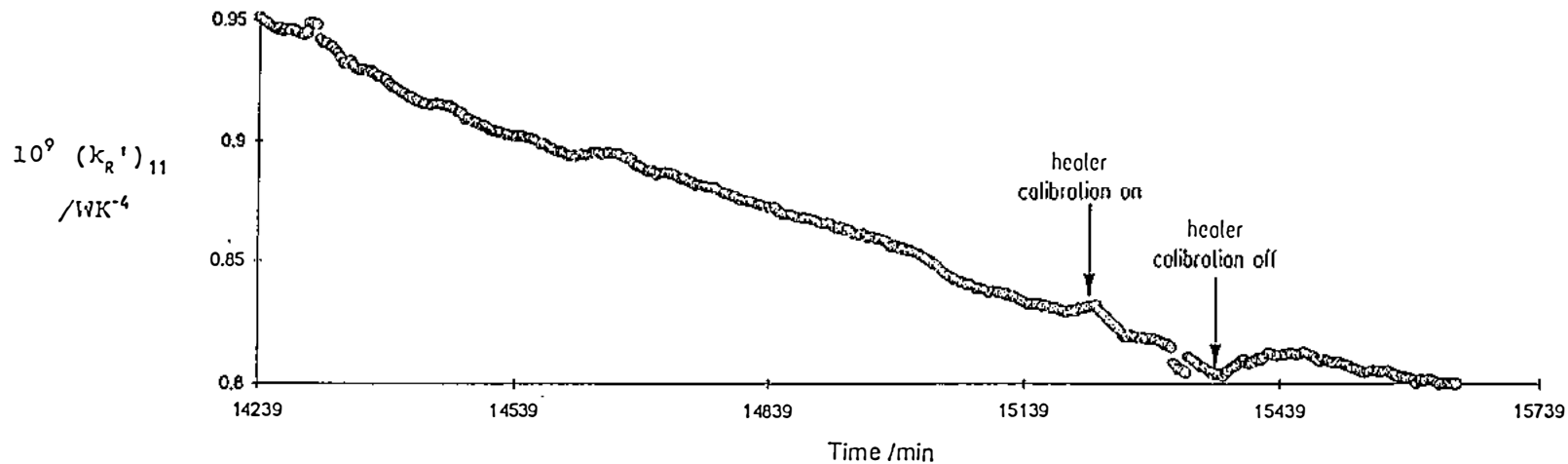


Fig 3B. The lower bound heat transfer coefficient,  $(k_R')_{11}$ , as a function of time for the section of data for Cell 4 illustrated in Fig 2B.

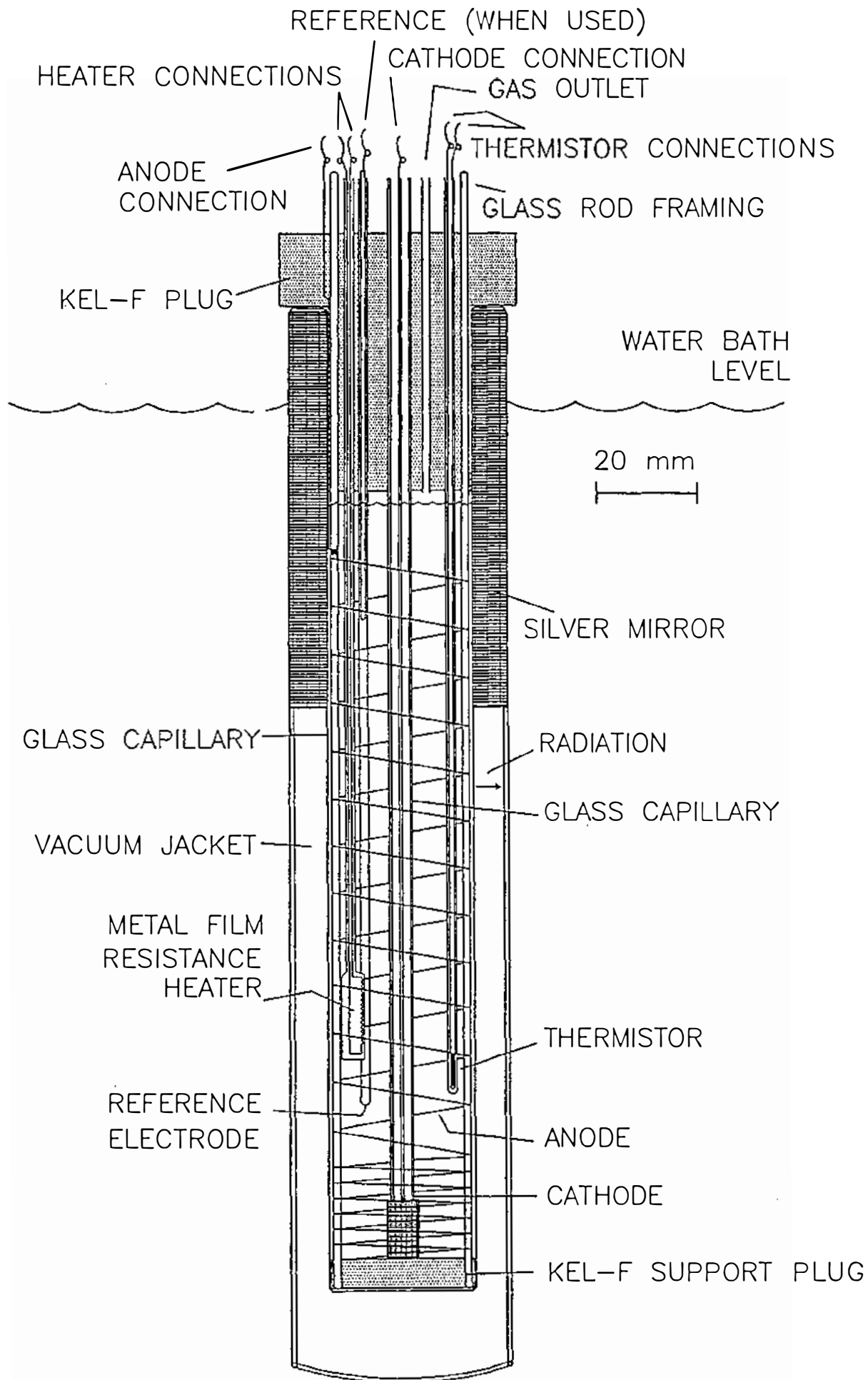


Fig 4A. The cell design used in current investigations at IMRA, Europe.



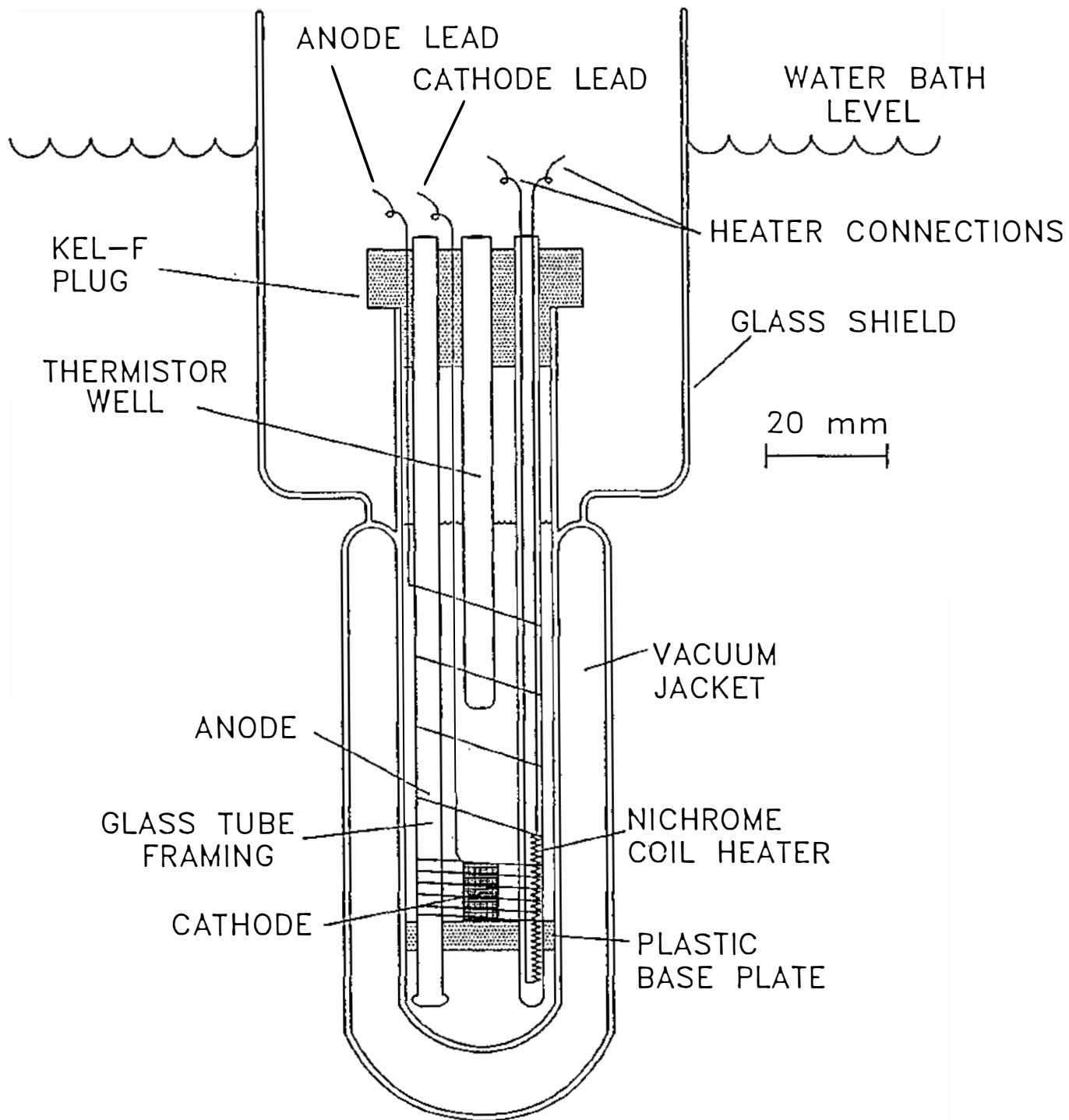


Fig 4B. The cell design used in the investigations at Harwell.

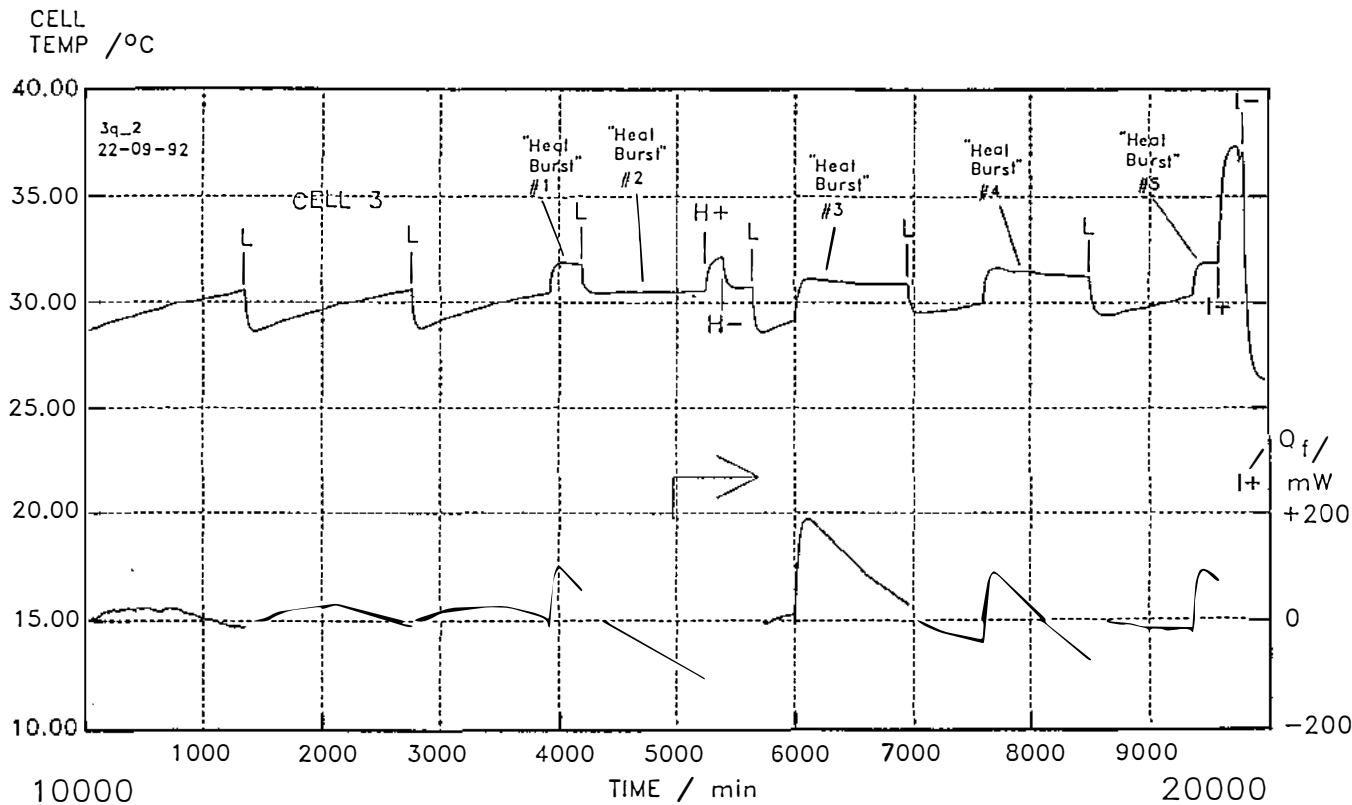


Fig 5A. The rate of excess enthalpy generation in Cell 3 derived using the lower bound heat transfer coefficients calculated according to the procedure outlined in the main text.

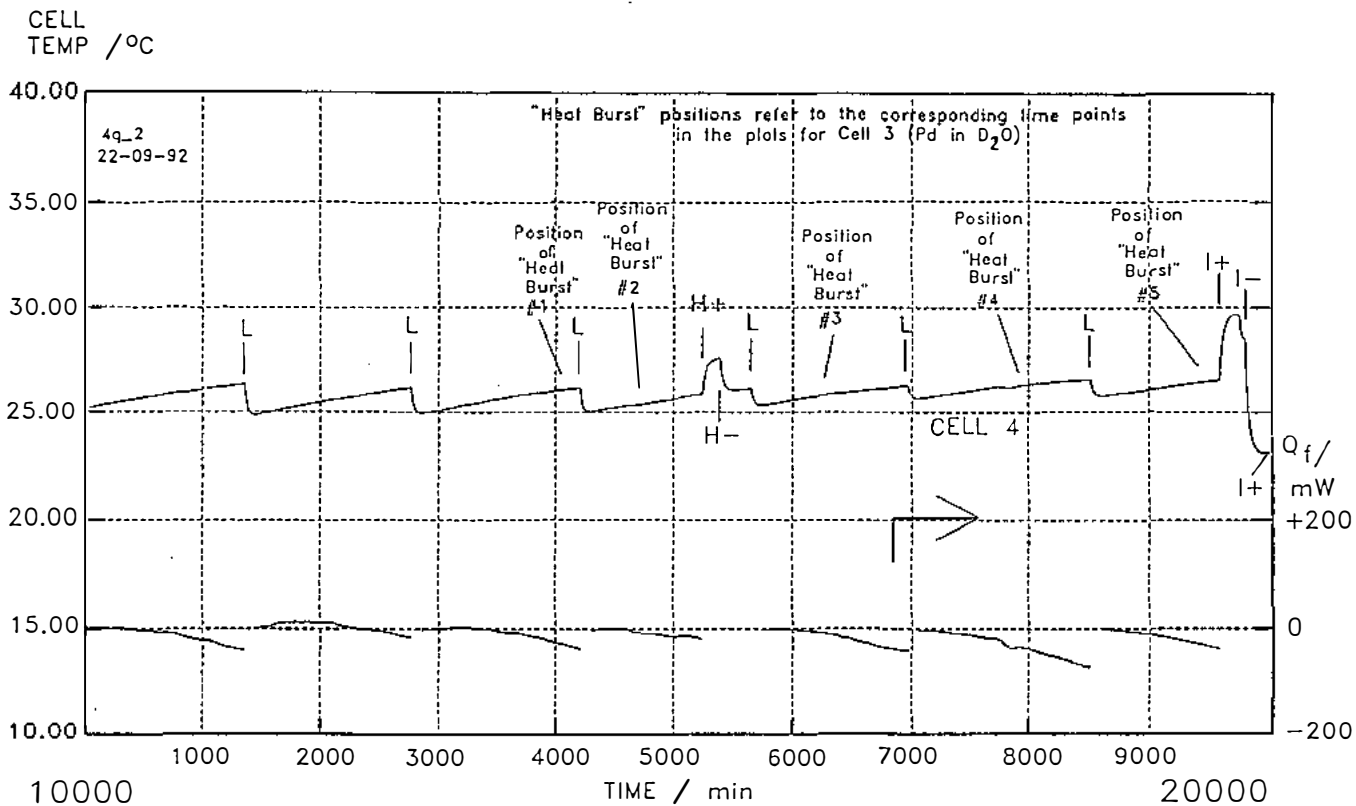


Fig 5B. The rate of excess enthalpy generation in Cell 4 derived using the lower bound heat transfer coefficients calculated according to the procedure outlined in the main text.

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