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Proceedings: EPRI-NSF Workshop on Anomalous Effects in Deuterided Metals

October 16-18, 1989
Washington, D.C.

Note: This document has been prepared for workshop attendees and is not intended for wide distribution.

REPORT SUMMARY

Proceedings: Workshop on Anomalous Effects in Deuterided Metals

Attempts to confirm Fleischmann and Pons's observations of cold fusion phenomena have met with inconsistent results. This second workshop on this topic brought together skeptics and advocates to facilitate communication, to examine closely the experimental results, and to identify research issues.

BACKGROUND The majority of attempts to confirm cold fusion phenomena have been unsuccessful. Although some researchers have confirmed portions of the Fleischmann and Pons experiment, these results have been sporadic and difficult to reproduce. The first workshop on this topic, sponsored by the Department of Energy, was held in May 1989 in Santa Fe, New Mexico.

OBJECTIVES

- To facilitate communication and collaboration among researchers from different laboratories/disciplines
- To evaluate data gathered since the Santa Fe Workshop
- To consider possible theoretical explanations of the anomalous effects and the implication of these explanations for future research

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APPROACH As a follow-up to the Santa Fe Meeting, the National Science Foundation and EPRI cosponsored a workshop October 16-18, 1989, in Washington, D.C. Thirty presentations by workshop participants addressed issues of nuclear byproducts, excess heat, and possible theoretical mechanisms for cold fusion.

Three subgroups met separately to consider these issues and make recommendations for future experiments and other research in these areas.

KEY POINTS

- The scientific and/or technological significance of cold fusion ultimately will be determined experimentally.
- Procedures must be developed to facilitate reproducibility of an individual laboratory's results by other laboratories.
- Collaboration among researchers from laboratories reporting positive results and those reporting negative results is critical to efforts to evaluate the anomalous effects.
- A convincing set of experimental data should include positive, nonsporadic, simultaneous measurements of excess heat and nuclear byproducts.

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ABSTRACT

The Workshop on Anamalous Effects in Deuterated Metals was held October 16-18, 1989 in Washington, D.C. The workshop was cosponsored by the Electric Power Research Institute and the National Science Foundation.

The objectives of the workshop were to bring together skeptics and advocates to examine closely the anomalous effects reported by researchers who have attempted to confirm the cold fusion phenomena observed by Fleischmann and Pons and to consider possible theoretical explanations of the anomalous effects and their implications for future research. Key steps required to remove the ambiguities surrounding cold fusion were identified and proposed, including the establishment of procedures to facilitate the replication of one individual laboratory's results by other laboratories and collaboration among researchers through the exchange of personnel and experiments.

Presentations addressed issues of nuclear byproducts, excess heat, and possible theoretical mechanisms. Following the formal presentations a series of shorter presentations were given on more recent results. Subsequently three subgroups met to consider these topics and made recommendations for future experiments and other research in these areas.

These Proceedings contain papers submitted by authors of 30 presentations made at the workshop, the discussions that followed each presentation, and summaries prepared by the session chairs.

EDITORIAL PERSPECTIVE

This Proceedings is an outcome of a workshop cosponsored by EPRI and the National Science Foundation (NSF) on the controversial topic of "cold fusion" research. This workshop, held October 16-18, 1989, was the first forum that succeeded in achieving a frank and open scientific discussion on the controversial findings reported by Pons and Fleischman and the various attempts to explain them. In addition, considerable insight was gained about how the experimental efforts could be improved. This aspect of the meeting's success is documented in this Proceedings, especially in the discussions and reports of the breakout sessions.

The assembly of this Proceedings has been the result of considerable effort by several members of the editorial committee. We were ably assisted by Henry Aeroeste and Carolee DeWitt, who provided scientific and production editing support, respectively. Raw transcripts of the discussions were provided by AAA Capital; these were edited by John Appleby with support from Henry Aeroeste.

Credits and thanks for the sponsorship of this workshop go to the management of NSF and EPRI who were willing to make the session possible even in the face of considerable controversy. The success of the meeting, however, was the result of the participants. A very high degree of professionalism was exhibited by all in attendance, and both skeptics and advocates engaged in constructive discussions.

The passage of time between the workshop and publication of this Proceedings has provided some additional perspective on this subject. Some of the measurements reported herein appear to be artifacts, unreproducible results, or mistakes. At this time, no clear evidence exists that "excess heat" is a result of a nuclear process. In general, the search for the kernels of real data has been difficult, and the relationships between all the anomalous effects are not yet understood. The final chapter of this saga is still to be written. My hope is that this Proceedings will help those interested in the history of this controversial subject better understand both the degree of scientific uncertainty and the chaotic state of knowledge that existed at the time this workshop was held.

Thomas R. Schneider
Managing Editor

Subsequent Cold Fusion Conferences

1st Annual Conference on Cold Fusion: Conference Proceedings, March 28-31, 1990, Salt Lake City, Utah, National Cold Fusion Institute.

Anomalous Nuclear Effects in Deuterium/Solid Systems: AIP Conference Proceedings 228, 1990, Provo, Utah, Ed: Steven E. Jones, Franco Scaramuzzi, and David Worledge.

The Science of Cold Fusion: Proceedings of the 2nd Annual Conference on Cold Fusion, June 29-July 4, 1991, Como, Italy, Ed: T. Bressani, E. Del Giudici, and G. Preparata.

Frontiers of Cold Fusion: Proceedings of the 3rd Annual Conference on Cold Fusion, October 21-25, 1992, Nagoya, Japan, Ed: H. Ikegami.

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Part 1

OVERVIEW

Section 1

REMARKS OF DR. EDWARD TELLER: ANOMALOUS EFFECTS ON DEUTERIDED METAL

REMARKS OF DR. EDWARD TELLER: ANOMALOUS EFFECTS ON DEUTERIDED METAL

We are further than ever from a real agreement on cold fusion. What has been seen has a wide divergence in results. I do not remember any case in my lifetime in science when so many experts have differed for such a long time on such relatively simple and inexpensive experiments. We are seeing a great deal of variability in the results -- whether due to surface effects or cracks or small changes in some unknown parameter. The experiments differ in many more ways than a simple theorist can explain.

I feel like the visitor looking at the giraffe and concluding, "there ain't no such animal." According to nuclear theory -- from the point of view of the Gamow factor -- there cannot be such an effect. The Gamow factor is not as simple as it is normally considered. Indeed, one must consider the temperature average over the Gamow factors. But before the hydrogen nuclei really have a chance of interacting with each other, they must be within a fraction of an angstrom and at that point the Gamow factor has a value of about 10^{-50}. On that basis alone, what we are seeing must be a series of mistakes.

But this is not the end of the controversy. Some of the good experiments show that something is really wrong with the branching of $D+D \rightarrow T + H$ and $D+D \rightarrow He^3 + n$. While I will not exclude a small variation in the ratio, the actual value reported is 10^8! Proton producing reactions (the Tritium branch) being 10^8 times more likely than neutron producing reactions. This is simply out of the question if D-D fusion is what is happening.

However, the history of science and experimental physics is full of examples of predictions that things are impossible and yet they have happened. I remember what Ernest Lawrence once said about me: "When Teller says it is impossible, he is frequently wrong. When he says it can be done, he is always right."

But what if we are presented with the fact that the results are correct? Then we will have to ask ourselves what are the minimum changes which we need to make in nuclear physics to explain the facts. If the giraffe exists, how does his heart pump blood into his brain? If the results are correct, then you must assume that nucleons can interact not just when they touch. We need to be able to explain how the nucleons interact at distances as great as 1/10 of an angstrom.

I think it would help if we postulated that the nuclei can interact at 10^4 nuclear radii and that the interaction is not through tunnelling but some exchange of "particles" which can extend outside of the nucleus. It will be remarkable but not impossible that "quarks" could exchange or interact at 10^{-9} cm with very low probability. This would be a low probability but still much greater than the Gamow factor. The probability that this could result in cold fusion is possible even if it is unlikely. If there is such an effect, we will then learn something very important. This would be a scientific discovery of the first order, the kind for which we are willing to spend $5x10^9$ dollars (SSC).

I therefore applaud the National Science Foundation and the Electric Power Research Institute for maintaining enough interest and enough support so that a real clarification of the apparent contradictions can be pursued. If that clarification would lead to something on which we can agree and to a reaction probability which is small, but much bigger than the Gamow factor would allow, this would be a great discovery. Perhaps a neutral particle of small mass and marginal stability is catalyzing the reaction.

You will have not modified any strong nuclear reactions, but you may have opened up an interesting new field (i.e., the very improbable actions of nucleii on each other. So, I am arguing for a continuation of an effort, primarily for the sake of pure science. And, of course, where there is pure science, sometimes, at an unknown point, applications may also follow.

But, according to my hunch, this is a very unclear and low probability road into a thoroughly new area. The low probability has to be balanced against the great novelty. But to think beyond that and ask what is the practical application, what this very unknown area of nuclear physics may produce, that I claim, is completely premature.

Thank you very much.

Section 2

ELECTROCHEMISTRY OF THE PALLADIUM D_2O SYSTEM

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ELECTROCHEMISTRY OF THE PALLADIUM D_2O SYSTEM

Nathan Lewis
Department of Chemistry, California Institute of Technology

First, I would like to express my thanks to the organizers of the workshop for allowing me to describe my viewpoint concerning the electrochemistry of the palladium-D_2O system. My task is to describe it without taking a stand for or against the alleged phenomena which we are here to discuss. I was told by the organizers that my role was not to present negative data but to point out some of the key concepts and possible problems in electrochemistry as it applies to cold fusion. Therefore, my presentation is intended be of a pedagogical character, but it will not educate the electrochemists in the audience. However, I hope that it will provide some background to the physicists and others who may not be very familiar with the electrochemical details. I hope to demonstrate what has been measured, what has not been measured, what controls are needed, and what other issues exist, particularly in respect to the electrochemical charging of palladium cathodes with deuterium, to measuring the heat flux, and to measuring separation factors for the isotopes of hydrogen.

A substantial amount of hearsay and rumors have been heard concerning what might occur at this meeting and also concerning the citing of positive confirming results based on the work of laboratories whose results have not been discussed in scientific meetings or written up in peer-reviewed journals. I believe that we must avoid any of these pitfalls. Since I must be objective, I will discuss only those things which I feel that I definitely know, and which will therefore be from my own direct experience in my laboratory. I hope that the same philosophy will be adopted in other contributions to this workshop.

The electrolysis of water requires the application of a current and a voltage across two electrodes. A constant current, a constant voltage, or indeed a constant power, may be applied, depending on the source. The application of alternative parameters will require different measurements and measuring instruments. In addition, since different losses occur in different parts of the electrical circuit, the potential drops in the various circuit elements should be simultaneously measured. While electrochemists know the crucial role which the potential of an electrode plays, it has nevertheless been rare when the researchers working in this area have reported the values of the individual electrical potentials in their circuit elements. Usually, only the total applied cell voltage has been measured. This can be a great source of uncertainty in comparing experiments. Hence, the individual potential differences should be carefully documented by all workers in this field in the future. Measurement of the electrical power delivered to the cell does not appear to be too complicated. However, if one is searching for small differences between the input power and the heat output, it turns out to be not quite so straightforward. Because of the experimental difficulties which are invariably involved in the calorimetric measurements, the facts as promoted by the popular press are certainly different from the real-time experimental data.

Accordingly, I will present some of the published experimental data on this subject, which will give a good impression of the magnitude of the effects we may be considering. The amounts of excess heat claimed vary from factors of 10% to factors of 400% or 100%. The size of such factors makes a large difference in the design of the experiments and in the equipment used. In short, we must appreciate what we are looking for in terms of heat detection.

The so-called isotope separation factors are also important. When water is electrolyzed to hydrogen isotopes and oxygen, it becomes enriched in the heavier isotope. This results from kinetic effects resulting from the different reaction activation energies, which depend on the zero-point energies, hence on the vibration frequencies, of the different isotopes, and on the complementary effects of nuclear tunnelling. These inevitably lead to a concentration of the heaviest isotope in the residue. This effect may therefore lead to the detection of tritium. If tritium is detected in large amounts, this cannot be explained by these kinetic effects alone. If very large effects occur, amounting to factors of a million or more, these cannot be obtained as a result of electrolytic enrichment. However, enrichment factors on the order of 2 to 3 certainly are within what one might expect from this mechanism. These facts will not be new for the electrochemists, or for those who routinely assay tritium.

In characteristic experiments, one can either apply a known voltage across the two electrodes and measure the corresponding current, or vice versa. In all cases, there will be an electrical lead resistance, and a resistance in the palladium cathode, which varies depending on its hydrogen or deuterium content. There will be a solution resistance, as shown. There will be an interfacial resistance at both electrodes, which derives from the existence of an electrochemical reaction, which is faradaic, rather than ohmic. In other words, unlike those of the other elements, its resistance varies with the applied current or voltage. However, for convenience the interfacial resistances can be expressed as an ohmic resistance at any given current density. As one would expect, all the above resistances will be in series, so that the largest values will dominate in the overall voltage drop. Thus, the component which contributes to the largest value must be determined. In a typical cell of Fleischmann-Pons type, the resistance in the leads and in the palladium itself will generally be unimportant. The most important factors contributing to the voltage drop in the cell will be the solution resistance, and probably more important, the interfacial resistance at each of the two electrodes. Measurement of the interfacial component of the voltage drop is often measured by current interruption.

Voltage drop resulting from ohmic resistance decays immediately, whereas that from faradaic and diffusion processes decays more slowly. One needs to know the potential of the working cathode (or anode) relative to some reference potential, which is typically zero on the standard hydrogen electrode scale, i.e, the reversible hydrogen electrode at a pH equal to zero. It is difficult to give an absolute indication of this potential, but the best values lie between +4.5 V and +4.7 V versus the vacuum level. One can also measure the electrode potential versus a standard electrode whose value is pH independent, or on the normal hydrogen scale, which is measured at the same pH as the experiment. This scale is the most convenient for general use with hydrogen or oxygen electrode systems, and it will be used in any subsequent discussions. It is important to establish the interfacial potential of the electrodes relative to this value. In practical cell designs, it is also important to determine the solution resistance.

Equipment and experiments may differ, but in a typical case the lead resistances are small, generally less than 1 Ω. The palladium electrode resistance is 9.9×10^{-6} Ω-cm for the pure metal and 1.7×10^{-5} Ω-cm for the composition $PdD_{0.8}$. Thus, the resistance of a 0.2 cm diameter, 10 cm long rod will lie between 3×10^{-3} and 6×10^{-3} Ω, depending on its loading. This change in resistance may be used to measure the loading, but I believe that it is better to remove the palladium from the cell and desorb the deuterium at high temperature to obtain a reliable value of the composition.

Therefore, as is the case of the leads, the palladium cathode resistance is small. In constrast, the interfacial resistance, which varies with the current density, can lie between about 1 and perhaps 100 Ω. With typical electrodes and current densities, the interfacial voltage drop may be between 1.0 and 1.5 V. Electrochemists call this voltage drop the kinetic overpotential, and it represents the irreversible work which is necessary to pass a given current to produce deuterium and oxygen from D_2O at a given rate. The reaction is catalytic, with the result that the ease of reaction, which is to say the overpotential at a given current density, varies with the electrode material. Palladium and platinum surfaces are particularly effective for hydrogen or deuterium evolution. Platinum is one of the best surfaces for oxygen evolution, but this reaction occurs at higher overpotentials than the corresponding hydrogen process.

The solution resistance will generally also be quite high. That for 0.0858 M LiOH is 49 Ω-cm. The corresponding value for LiOD has been measured by Dr. Martin at Texas A&M University, and it is about 50% higher than that of LiOH over a wide concentration range. Thus, a typical value for 0.0858 M solution is 74 Ω-cm, and in a typical cell with 0.5 cm^2 electrodes separated by a distance of 0.2 cm, the solution resistance would be about 60 Ω, which would increase if the interelectrode separation increased. Hence, the solution resistance will predominate at low current density, whereas the Faradaic resistance should predominate at high current density. Another important point is that if experiments in LiOH and LiOD solutions are to be compared, we should remember that the Joule heating will be 50% greater in the latter at the same concentration. This is important in the design of blank experiments.

For a pH 3 solution dominated by sodium and sulfate ions at 0.035 M, the effect of proton conductivity (at the equivalent concentration of about 10^{-3} M) will be small. This electrolyte is the geological "Mother Earth" composition used by Jones. The correct IR drop for two 1.7 cm^2 electrodes separated by 2 cm, is on the order of 200 Ω. Fig. 3 shows the electroactive materials present in this electrolyte. The electrochemical potentials for their reactions as shown are expressed relative to the vacuum level. On the pH = 0 hydrogen electrode scale, the latter is +4.5-4.7 V. Ions present include Ti, Ni, Fe, H, Pd, and Au. The solution resistance is the most important voltage drop across the cell. The difference between the anode and cathode potentials is the much smaller difference between the interfacial potential drops. The actual values of the anodic and cathodic potentials will determine if the electroactive ions can indeed react at these electrodes. Thus, if we apply a constant voltage of, e.g., 5 V across the anode and the cathode, a current will flow. Its value will be adjusted by the solution resistance, and the current-dependent (i.e., potential-dependent) interfacial resistances, which themselves depend on the reactions taking place at the electrodes. The sum of the interfacial potentials and the IR drop will be equal to 5 V, but we cannot easily predict the values which the interfacial potential differences will take up. Therefore, we cannot absolutely say whether or not Ni^{2+} is being reduced to Ni^0, or indeed whether the cathode was more negative than this potential. Equally, we cannot say *a priori* whether the anode is oxidizing water to oxygen. Hence, for a given applied cell voltage the specific electrochemical reactions occurring at a given cathode at a given applied voltage depend on the spacing, on the geometry of the cell, and on the conductivity of the electrolyte.

At constant current (galvanostatic conditions) the situation is simplified. The voltage drop across the electrolyte double layers is fixed, and the interfacial resistances adjust themselves to correspond to the currents flowing, which represent the rates of the electrochemical reactions at the electrodes. This is one reason why electrochemists often prefer to operate experiments under galvanostatic control, since the reactions rates are then independent of the solution resistance.

The rates of many reactions are controlled by mass transport. In the example quoted, Ni^{2+} must diffuse to the electrode surface to discharge to Ni^0. Typical diffusion coefficients are in the range 10^{-5} to 10^{-6} cm^2/sec. This means that expressed in current terms, the diffusion rate of a typical ion in a stirred aqueous solution is about equal (in A/cm^2) to its concentration (in M/l). If the applied current density exceeds the maximum diffusion rate for a particular species, the potential of the cathode will move in a negative direction until a reaction is located which can be sustained. For example, if the applied current density is too large for the deposition of Ni^0 from Ni^{2+}, the electrode potential will go to the next potential range where reaction may occur, in this case, deposition of Fe^0 from Fe^{2+}. At this potential, both iron and nickel will be codeposited, with the latter under diffusion-limited conditions. It the current is too large to be sustained by both of these processes, along with any other cathodic processes occurring at even higher potentials, then the electrode will reach the hydrogen evolution potential. Under these conditions, gaseous hydrogen will be produced from water, and the trace metals will be codeposited. Hydrogen evolution is from water, which is present in overwhelming concentration and has an enhanced transport mechanism for H^+ and OH^- ions. Hence, no limiting current would be expected for this process in any reasonable current density range. The situation at the anode is similar for oxidative processes, with the anode ultimately reaching oxygen evolution at a sufficiently high current density. Again, this reaction will have no limiting current in the normal current density range. For information on transport limitation, electrochemists make measurements with a rotating disk electrode, which permits precise control of the steady-state diffusion layer thickness.

We will now turn to a further discussion of the implications of electrode potential. The Nernst equation for potential contains the standard reversible thermodynamic value of the potential (in cV) for a process (corresponding to $-\Delta G°/nF$, where $\Delta G°$ is the standard free energy of the process, n is the number of electrons involved, and F is the Faraday), corrected for the free energy change as a function of concentration. Since free energy and concentration are related logarithmically, a 10-fold change in the latter results in a 60 mV change in reversible potential at 298°K.

In practice, these reversible potentials can be very misleading. If one measures the potential of the palladium cathode operating a high current density for hydrogen evolution, one finds that it is -0.8 V against the reversible hydrogen electrode in the same solution, i.e., the potential at which hydrogen should be evolved according to the Nernst equation.

There is also controversy regarding the actual estimate of the internal pressure of deuterium gas inside the Pd. One often hears figures as high as 10^{27} atm quoted. I would now like to tell you how this figure was obtained and what it really means physically. A typical experiment uses a two-compartment electrochemical cell with a porous separator between the compartments. On one side is a palladium electrode in the electrolyte, which is saturated with hydrogen at 1 atm. pressure; on the other side is a high-surface-area (hence, highly catalytic) platinum electrode, also in contact with 1 atm of hydrogen. No current flows in the system. The potential of the platinum electrode is that of the reversible hydrogen electrode in that electrolyte, which we may define as zero on our reference potential scale. If the potential of the palladium electrode is -0.8 V on this scale, the question one should then ask is, "Using the Nernst equation, what hydrogen pressure is necessary to make no net current flow for the 2-electron hydrogen reaction at an electrode at -0.8 V on the hydrogen electrode scale?" The answer is 10^{27} atm. Clearly, this situation is absurd, since the atmosphere above the palladium electrode is only at 1 atm pressure. When current is flowing, the potential which is measured bears no relation to the pressure of the hydrogen produced at the surface of the electrode, or the pressure inside the electrode. Similarly, the pressure outside the system may indeed be considerably less than the pressure at the surface of the electrode, where supersaturation may take place due to gas bubble formation. The true hydrogen pressure at the surface of, or in the electrode, may be arbitrarily big or small depending on the details of the process.

The potential which is measured gives information on the phenomenon known to electrochemists as overpotential. It indicates that the electrochemistry is a high energy process, in which an electrical potential can be used to drive a reaction as an alternative to using high chemical potentials, e.g., high pressures. It is easy to apply 0.8 V, and for example, maintain zinc in a reduced state, whereas it is much more difficult to perform the equivalent via the effects of chemical potential, which would require a hydrogen pressure of 10^{27} atm.

Potentials are generally measured relative to a reference electrode with current flowing, usually under galvanostatic conditions. Alternatively, a potentiostat may be used to measure current flowing as a function of the applied potential, again relative to the reference electrode. This instrument operates by electronically adjusting the current to maintain the potential of the working electrode at the desired value. The value of the potential measured will contain the value of the interfacial potential, together with the free energy difference between the working electrode (in this case, a palladium cathode and the reference electrode). It will also contain any potential drop in the solution, or uncompensated solution resistance, which can be minimized by a special reference electrode design. The uncompensated solution resistance may be measured manually or by electronic feedback built into the potentiostat. If, for example, 0.8 V is applied to the cathode, and if the effect of the uncompensated solution resistance is determined to be 0.2 V, then the remaining 0.6 V is a combination of the free energy differences and the interfacial potential difference. The effect of the latter can be eliminated by measuring the potential after current interruption, which shows an instantaneous drop for the effect of solution resistance between the cathode and the reference electrode, and a slower decay for the interfacial potential difference. Thus, we are left with the potential value corresponding to the free energy difference between the palladium cathode and the reference electrode. This will allow us to determine the hydrogen pressure in the palladium alloy phase.

In our laboratory, we obtained potentiostatic data for a palladium cathode in 0.1 M LiOD relative to a convenient reference, the palladium-deuterium electrode charged to the $\alpha-\beta$ phase equilibrium, rather than to a reversible hydrogen (deuterium) electrode. The former has a reversible potential of +50 mV relative to the latter. The results showed the overall current potential relationship both uncorrected, and corrected for solution resistance. After current interruption, we determined the free energy difference between the cathode and the reference electrode. It was shown that the interfacial potential difference was quite small, and that the free energy difference is the predominant potential term in this case, representing -0.7 to -0.8 V at a current density of 60 mA/cm^2. This value represents the minimum free energy difference to maintain the palladium-deuterium phase at equilibrium with no current flowing. This free energy difference tells us which electrochemical reactions are thermodynamically possible under these conditions.

Most of the University of Utah electrochemical experiments used 0.1 M LiOD as electrolyte. However, Brigham Young University's work used a 1.0 mM acidic solution. In the first case, a basic solution is used, which contains about 10^{-13} M D^+ ion, and correspondingly 10^{-1} M OD^- ion. In the second, D^+ ion is 10^{-3} M. Both solutions contain about 55 M D_2O, which supports most of the cathodic process. In both electrolytes, the atomic fraction of deuterium in the palladium cathode can be increased from 0.8 to 0.85 by continued electrolysis. This has often been reported by measuring the weight change in the system, but this method is likely to be inaccurate, since other material can deposit on the palladium under cathodic conditions. The most effective method of determining the composition is by degassing the electrode, with volumetric or pressure determination of the gas evolved.

If we now turn to calorimetry, I would like to discuss the heat flux calculations which must be carried out in open and closed systems. In a closed system, in which the only reactions are decomposition of heavy water to deuterium and oxygen, followed by their recombination, the voltage across the cell terminals multiplied by the total cell current indicates the heat entering the cell. According to the first law of thermodynamics and in the absence of any other effects, this value should equal the heat leaving the calorimeter.

In an open system, the applied voltage is partitioned into two quantities. The first part, when multiplied by the total current, represents the energy flow in the form of heat into the cell. The second part is the energy which is required to form deuterium at the cathode and oxygen at the anode, which escape from the open system. The standard enthalpy of dissociation of D_2O to give D_2 and O_2 is well known. This value can be converted to an equivalent voltage necessary to electrolyze D_2O by dividing the molar heat of dissociation by the number of electrons per mole (i.e., two) and the value of the Faraday. The result is 1.48 V for liquid H_2O, and 1.527 V for liquid D_2O, under standard thermodynamic conditions at 25°C. This equivalent voltage, again multiplied by the cell current, must be subtracted from the total energy supplied to the cell to determine the output heat flux.

The difference between open and closed cases therefore concerns how much of the electric input power is partitioned into the energy flux from the cell and into the energy flux escaping with the evolved gases. If the system is closed, all of the input power appears as heat energy escaping from the calorimeter. If the system is open, an amount of energy up to a maximum value, depending on the electrolysis efficiency, can escape with the gases produced. Thus, the correction would be $1.527 \cdot I$, where I is the total cell current, assuming that all of the electrode reaction represents water dissociation at 100% efficiency, with no recombination. Measurements of the latter have normally shown it to be very small. It can certainly depend on cell geometry, and on whether a separator is used between the electrodes. I do not intend to speculate on whether recombination can increase to the extent of causing a substantial error. I will simply note that it is possible. It can in principle occur via two methods. First, deuterium can be transferred via the electrolyte and be oxidized at the anode. Similarly, oxygen can be transferred to the cathode and there be reduced. Secondly, instead of being electrochemical, recombination can be chemical, taking place on catalytic surfaces, such as the sides of the cell where platinum or palladium may be deposited. If the fraction of the gases which recombine is x, then the correction for the amount of energy lost via the gases evolved will be $1.527 \cdot I(1-x)$.

Data on heat fluxes were reported in the original Utah work. I believe that it is important to understand this data analysis, because the raw data is not widely available and has not been published to date. Furthermore, the data analysis method also is not widely known, which leads to confusion regarding the magnitude of the effects actually observed that have been ascribed to anomalous excess heating. In fact, highly exaggerated estimates of excess power have appeared both in the popular press and in some of the scientific literature based on interpretations of the meaning of the originally reported excess power figures. For example, are the anomalous effects 1000% or 400% of the heat flux into the cell, or less than these values? Based on the published data of Fleischmann and Pons, the results show that often the differences being determined are very small, and they will therefore require very accurate calorimetry for a precise determination. Since both Professors Pons and Fleischmann are here, I would like to know whether my interpretation is consistent with their actual analysis method or if we have made an error in these calculations. (Fleischmann and Pons nod in agreement.) The widely quoted 400% and 1000% excess power numbers were calculated based on the assumption that the reactions can be carried out at 0.5 V, which assumes no 1R, with one electrode evolving deuterian and the other oxidizing it. This was based on highly questionable assumptions and was never measured in actual experiments. The measured excesses are actually very small (10-30% of total input power) in most instances, and in most cases, the observed heating power is less than the total input power. Only if no recombination is established, and accurate calibration is demonstrated, can these values be considered trustworthy. It would be far better to build a calorimeter in which the claimed 50 W of excess power yielded a result that was a factor of 2 to 3 higher than the calibration curve, not a mere 5-10% higher. This should be possible to construct and will be crucial if one is to demonstrate unambiguously a substantial excess-heat effort. This is a challenge which has not been met to date, but I hope that it will be met very shortly in order to resolve this issue. In my view, much of the data obtained has been insufficiently accurate to determine such small differences. Initial data show the charging of a palladium cathode with deuterium, which presumably was not producing excess heat, because of the time required for complete charging. In order to claim that excess heat is produced, the calorimeter constant must be claimed to be indeed a constant, and its value must be known with a high precision. Significant errors can occur in calorimetry, and they must be very carefully taken into account in interpreting measurements.

This is particularly evident when no recombination is assumed in open cells. For example, at low power, the overall cell voltage may be 3V; thus, after subtraction of the voltage equivalent to the heat of dissociation of D_2O, the heat flux entering the cell will be approximately 1.5-I, where I is the cell current, assuming no recombination. This represents a total change of 50%. Let us consider that a heater is used to model the cell. If we apply the same electrical power to the heater as that applied to the cell, then if the cell showed no recombination, the heat flux from the cell would be 50% of that from the heater. The remaining energy would escape in the evolving gases. As the power into the cell (i.e., the applied current and voltage) is increased, the fraction of energy represented by that in the evolving gases will proportionately decrease. In other words, at progressively higher voltages, 1.54 V represents a smaller fraction of the total cell voltage. Thus, performing the same experiment with the power into the heater equal to the power into the cell at these higher voltages, the heat flux from the cell should approach closer to the heater calibration line. Because the effective interfacial resistance is current-dependent, the data should not fall on a straight line. As a result, I would question the precision and accuracy of the data points in this work, which was reported in a highly publicized set of experiments as having confirmed an excess-power production rate in heavy water.

In our own calorimeters, we have maintained the current constant and adjust the heater power to determine the calibration constant as a function of time. These indicate that as gas is evolved, heat is in fact lost more effectively. Finally, for each point the system appears to approach a steady state. The question at issue is whether the change in calibration constant can be distinguished from an effect which is interpreted as a change in the heat produced by the cell. There are therefore two unknowns, namely the heat produced and the calibration constant. In order to uncategorically determine both unknowns, a calibration must be carried out at each data point. To date, this has not been generally done in most systems.

Some new data were very recently obtained in a closed system calorimeter in our laboratory, and they have only been obtained in one experiment, so far without an H_2O control experiment. Since the system is closed, no thermodynamic corrections are required for D_2O dissociation. In the calorimeter, the temperature of an internal water bath is accurately measured relative to an external one using thermocouples. The system is arranged so that the temperature differences are relatively large. After calibration, the current to the internal palladium-platinum electrolysis cell, which had a 4 mm diameter, 1 cm long cathode, is turned on. If the cell had been showing an anomalous heat flux, the point would be far beyond the calibration line. We did not observe this. The challenge in other work therefore lies in accurate calibration and proof of an effect for outside-of-system errors.

I would now like to consider the question of separation factors for deuterium and tritium. When water is electrolyzed, a kinetic isotope effect occurs, so that molecules of the lighter isotope are preferentially evolved. This effect was studied by Libby, and the process has been used for isotopic enrichment. As to the values of the kinetic separation factors of the different isotopes, much more information exists on H_2O/HD (and ultimately HD/D_2 separation factors) in H_2O/D_2O mixtures than on the corresponding D_2/DT and DT/T_2 values. Three separation factors are of interest. One is the ratio of DT in the solution compared with that in the solid palladium phase. The next is the corresponding ratio in the electrolyte compared with that in the gas phase, and the third is that in the gas compared with that in the solid phase.

The known HD separation factors are to be expected to be greater than the corresponding DT values, because of the smaller mass ratio of the latter. The most relevant DT value would be that in the gas phase compared with that in the electrolyte, since this is of primary experimental interest. In acidic solution, the HD value is approximately 5, and that for DT would be expected to be about 2. For alkaline solution, we can use Fleischmann and Dandepani's 1974 data, which show that the HD separation factor between the electrolyte and gas phases is somewhat a function of potential. For a 1 M base, the corresponding values are 8 to 10. No literature data are available for DT, but a reasonable number would be approximately 3, which would depend somewhat on interfacial potential, i.e., on current density. Thus, if the value is 3, electrolysis of 1% of a dilute tritium-containing electrolyte without makeup would cause a tritium enrichment by a factor of 1.007. The corresponding figures for electrolysis of 10% of the solution would be 1.07; for 50%, 1.59, for 90%, 4.64, and for 99%, 21.5. If the solutions are made up to their original volume, which is normally the case in electrolysis experiments, then for electrolysis of 10% of the solution, tritium enrichment would be only 1.007; for 50%, 1.30; for 90%, 1.36; and for 99%, 1.21. The maximum value will be 1.38, corresponding to electrolysis of 81% of the solution. Thus, these numbers, even if they are approximate, set an upper limit on tritium enrichment by electrolysis. With 20 ml of electrolyte, adding 2 ml each day would result in a progressive enrichment of 1.06 in 8 days or 1.48 in 56 days. If we take the upper limit value of the separation factor, i.e., infinity, the enrichment each day would be by a factor of 1.1. Hence, after 8 days under these conditions, the enrichment would be 1.21, and 208 after 56 days, so it may be argued that extensive tritium enrichment results from some unusual change from the expected value of the separation factor. This subject therefore requires further investigation.

In concluding, I would hope that this presentation has indicated some of the pitfalls of this research.

DISCUSSION (LEWIS)

Schneider: One can speculate on reducing the input voltage to lower levels than those observed. Some of the fuel cell community feel that values as low as 0.2 V may be possible in a cell with a deuterium anode.

Lewis: I think that idea is a misconception, based on the experimental data that have been obtained for deuterium evolution on bulk palladium. The measured open-circuit polarization is about -0.8 V versus the deuterium electrode potential. I believe that this is a thermodynamic quantity, not an irreversible overpotential. The reaction therefore cannot proceed at overpotentials more positive than -0.8 V, according to the first law of thermodynamics.

Hoffman: Some of the deuterium, or tritium when it is produced, dissolves from the gas phase into the liquid electrolyte. This can be important in some types of experiment, particularly those with deuterium anodes, such as in Dr. McKubre's pressurized experiments at SRI.

Lewis: My analysis ignores any dissolved gas in the liquid phase. I also ignored any dissolved tritium in the palladium. I have assumed that the system is open, not closed, with evolving deuterium and oxygen. Other types of electrode could be used in closed systems.

Yeager: The isotope separation factors, as well as the overvoltages, are extraordinarily sensitive to a number of variables that have not been emphasized. The surface topography of the electrode is particularly important. Literature values of electrochemical isotope separation factors have often not been measured under rigorous enough conditions.

Fleischmann: There are some mysteries concerning deuterium-tritium separation factors. The values obtained in industrial processes tend to be confidential. It would be useful to have access to the separation factor values.

Bockris: We have measured values of 1.7 to 2.2. It is particularly interesting that deuterium preferentially concentrates in palladium, which points to reverse isotope effects. It is also very difficult to understand a separation factor of two between the gas and liquid phases.

Jordan: Since this presentation was intended for non-electrochemists, it would be worth emphasizing that the pressure considerations which were discussed are all related to equilibrium electrodynamics. If there are overvoltage effects due to irreversible electron transfer, it is misleading to ascribe these as being equivalent to the effect of a higher deuterium partial pressure.

Lewis: The effects of overvoltage will simply further increase the electrode potentials beyond the reversible thermodynamic values. The essential factor is how high a voltage one has to apply to carry a given current on a palladium cathode.

Appleby: Do you have corresponding data for platinum?

Lewis: Not for this type of experiment.

Appleby: Platinum seems to have a higher overpotential than palladium at the same current density in the 1 A/cm^2 range. Palladium dissolves hydrogen or deuterium, whereas platinum does not. The effects observed on both metals involve mostly irreversible kinetic overpotential.

Lewis: That may be so, but my argument is essentially thermodynamic, involving the open-circuit potential difference between the actual electrode in the cell and the reference phase of the gas atmosphere.

Section 3

CALORIMETRY OF THE PALLADIUM-D-D_2O SYSTEM

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CALORIMETRY OF THE PALLADIUM-D-D_2O SYSTEM

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INTRODUCTION

The strange behavior of the isotopes of hydrogen dissolved in palladium under cathodic polarization is well documented(1). Fig. 1 illustrates a number of the important features of the discharge of D_2O and of D_2 evolution for electrolyses in alkaline media as well as of the dissolution of adsorbed D in the palladium lattice. At the reversible potential the initial state of reactions (i) a D_2O molecule interacting with its surroundings together with an electron in the Pd lattice) is in equilibrium with the final state (an adsorbed atom and a deuteroxide ion again interacting with their surroundings). For experiments close to atmospheric pressure the lattice is already in the β Pd-D phase. Increases in the difference of the galvani potential between the metal and the solution $|\Delta(\phi_m - \phi_s)|$ (shown here in a highly simplified form as a linear potential drop in potential across the Helmholtz double layer) from the value at the reversible potential stabilize the final state with respect to the initial state to an extent $\Delta(\phi_m - \phi_s)F$ joules $mole^{-1}$. The adsorbed atoms are therefore "driven" onto the surface and, in turn, the adsorbed species are "driven" into the FCC lattice, step (ii), where they exist as D^+ ions, almost certainly in the octahedral positions. The adsorbed species are desorbed in the further step (iii). At very negative potentials, the D^+ species behave as classical oscillators(2). A peculiarity of the Pd/D system as compared to Pd/H and Pd/T is that the diffusion coefficient of D exceeds that of either H or T!(3) It is tempting to attribute this phenomenon to the boson character of the particles but we do not wish to let our enthusiasms cloud our judgement - the phenomenon certainly requires further investigation.

The concentration of D^+ in the lattice under equilibrium conditions is already very high (D/Pd ≅ 0.6-0.7). The composition of the lattice at high negative potentials has still not been established with precision but it would be surprising if the D/Pd ratio did not approach unity under these conditions. The dominant effect of the increase in cathodic potential must, however, be an increase in the activity of the dissolved hydrogen. The activity will be determined under steady state conditions by the rates of steps (i), (iii), and (iv) but we will restrict attention here to a quasi-thermodynamic argument based on an hypothetical equilibrium of reactions(i) and (ii). For such an equilibrium we can equate the electrochemical potentials of the initial and final states

$$\bar{\mu}_{D^+,m} + \bar{\mu}_{OD^-,s} = \mu_{D_2O,s} \tag{1}$$

or

$$\mu_{D^+,m} + \phi_m F + \mu_{OD^-,s} - \phi_s F = \mu_{D_2O,s} \tag{2}$$

i.e.

$$\mu_{D^+,m} = \mu_{D_2O,s} + \mu_{OD^-,s} - (\phi_m - \phi_s)F \tag{3}$$

In this expression $\mu_{D_2O,s}$ and $\mu_{OD^-,s}$ will be close to the standard state values. It should be noted that $\mu_{D^+,m}$, $\mu_{OD^-,s}$, and $(\phi_m - \phi_s)$ are quantities which are not accessible to thermodynamic measurement but the change in chemical potential of the dissolved D^+, $\Delta\mu_{D^+,m}$ due to a change of the galvani potential potential difference $\Delta(\phi_m - \phi_s)$, from the value existing at the reversible potential is thermodynamically defined (as is $\Delta(\phi_m - \phi_s)$).

Values of $\Delta(\phi_m - \phi_s)$ as high as 0.8 V can be achieved using conventional electrochemical systems and values even higher (in excess of 2V) could be achieved under special conditions(4). While the energy values $\Delta(\phi_m - \phi_s)F$ may appear to be modest, they are, in fact, of astronomical magnitude. Thus, if one were to attempt to achieve the same activity of dissolved D^+ by the compression of D_2 using reaction steps (ii) and (iv) under equilibrium conditions (as is customary in heterogeneous catalysis) we would need to satisfy the condition

$$2\mu_{D^+,m} + 2\mu_{e,m} = \mu^{0}_{D_2,g} + RT \ln P_{D_2} \qquad (4)$$

where P_{D_2} is the fugacity of the gaseous D_2. We obtain

$$\mu_{D^+,m} = \mu^{0}_{D_2,g}/2 - \mu_{e,m} + RT/2 \ln P_{D_2} \qquad (5)$$

and, it can be seen that a 0.8 eV shift of the potential of the electrode corresponds to a $\cong 10^{27}$ fugacity of D_2:

$$0.8F = RT/2 \ln P_{D_2} \qquad (6)$$

Such high hydrostatic pressures are naturally not achievable on earth and, even if they were, other phenomena would intervene (formation of metallic D, collapse of the Pd lattice). The argument is instructive, however, from several points of view: in the first place it points to the importance of the "poisoning" of the desorption steps (iii) and (iv) (so as to drive (i) as close to equilibrium conditions as possible); secondly, it points to the special role of cathodic polarization in causing the "compression" of D^+ into the lattice; thirdly, it suggests that clusters of D^+must form in the lattice under such extreme conditions by analogy to the nucleation of metals. Such clustering may well be initiated at the octahedral sites which would distort so that these sites might then be more correctly described as being parts of dislocation loops.

The starting point for our investigation was the question: would it be possible to induce the established nuclear fusion reactions(5)

$$^{2}D + {}^{2}D = {}^{3}T + {}^{1}H + 4.03\ \text{MeV} \qquad (v)$$

$$^{2}D + {}^{2}D = {}^{3}He + n + 3.27\ \text{MeV} \qquad (vi)$$

under these conditions? We were naturally aware of the many reasons why this might not be possible. Our discussions always ended on the note: this experiment has a one in billion chance of success. Nevertheless, there were (and still are) a number of further factors which point to the possibility of inducing nuclear reactions. The dissolved D^+ is, in fact, a very high density, low ion temperature plasma existing in a high electron concentration. We can therefore pose the following conundrum: it would be expected that the s-electron density around the nuclei would be high but this would lead to the formation of D_2. As this is not observed the s-electron density must in fact be low. While we do not subscribe to the notion of the formation of heavy electrons, we recognize that the electron density in the clusters must be highly asymmetric and that it is necessary to develop a priori calculations about the many body problem (i.e. taking into account the presence of the lattice) before it is possible to make any predictions of the Coulomb repulsion and nuclear motion in the clusters contained in the host lattice. We also draw attention to two further relevant observations. Firstly, the source of the original reactions (v) and (vi)(5) appears to have been overlooked in all of the comment about our initial announcement(6,7). This neglect has no doubt been due to the change of terminology since the 1930's (deuterium was called diplogen and the deuteron was called the diplon at that time so that casual searches fail to reveal the early literature). Cloud chamber work(8,9) at the time of the discovery(5) showed quite clearly that low energy deuterons undergo at the least reaction (v). Secondly, it is known that high density low ion temperature D^+ plasmas induced by electron-cyclotron resonance in D_2 gas in magnetic mirror devices generate neutrons(10) presumably by reaction (vi). This observation too appears to have been forgotten.

It is now difficult to express our astonishment at our results as they became available: it became clear that there were only very low levels of radiation in the electrolysis and that reactions (v) and (vi) only took place to extremely small extents. Nevertheless excess enthalpy over and above that supplied to the cell for the electrolysis of D_2O

$$2D_2O \rightleftarrows 2D_2 + O_2 \qquad \text{(vii)}$$

was being generated and the magnitude of the excess enthalpy was such that it could not be explained by chemical reactions. It was also clear that it was necessary to carry out large numbers of experiments for long times (the median time scale for an experiment cycle is three months) in view of the irreproducibility of the phenomena. We therefore made the low cost calorimetric investigation of large numbers of electrodes our initial prime method of investigation and we give an account of this work in this report.

EXPERIMENTAL

Fig. 2 illustrates the simple single compartment Dewar cell calorimeter we have adopted for most of our work. The general principles underlying the design have been described elsewhere(11). The central palladium cathode was surrounded by an helical anode closely wound on glass rod supports and this ensured uniform charging of the cathode. Measurements using dye injection (tracer technique of chemical reaction engineering) have shown that at the minimum currents used in most of the experiments (200 mA) radial mixing is very rapid (time scale < 3 s). Axial mixing is somewhat slower(≅ 20 s) but,as heat injection into the system is axially uniform and, as the thermal relaxation time is ≅ 1600 s, the cells behave as well stirred tanks. In agreement with this prediction measurements with an array of 5 thermistors which could be displaced in the radial and axial directions have shown that the maximum temperature variation was ±0.01° except in contact with the bottom Kel F support where it reached 0.02°. All temperature measurements were made with specially calibrated thermistors (Thermometrics Ultrastable Thermoprobes, ≅ 10 kΩ, ±0.02% stability per year).

The cells were maintained in specially constructed thermostats (1/2" thick Plexiglas bath surrounded on 5 sides by 2" thick foam insulation bonded on both sides to aluminum foil, the whole structure being enclosed in a 1/16" thick sheet steel container); the water/air interface was allowed to evaporate freely. Stirring with oversized stirrer-temperature regulators ensured that the bath temperature could be controlled to ±0.01° of the set temperature (in the vicinity of 303.15K) throughout the whole space at depths greater than 0.5 cm below the water surface and to ± 0.003° at any given point. The water level in the thermostats was controlled using dosimeter pumps connected to a second thermostat. Up to 5 cells were maintained in each of 3 thermostats at any given time.

All experiments were carried out galvanostatically (Hi-Tek DT2101 potentiostats connected as galvanostats as shown in Fig. 3). The systems could be calibrated at any given operating point using metal film resistor chains in the cells (Digikey ±1% accuracy 5 x 20Ω). The procedure adopted was as follows: after the addition of D_2O (or of electrolyte following sampling for analysis for tritium or HDO) the system was allowed to equilibrate for at least 6 thermal relaxation times. A constant current was then applied to the resistor chain (again supplied by a potentiostat connected as a galvanostat) for 3 hours (i.e. > 6 thermal relaxation times) to give a temperature rise of $\cong 2^{\circ}$ above the sloping base line and this current was then switched off and the relaxation of the system to the original sloping base line was followed. Cell parameters were monitored every 5 minutes using Keithley Model 199 DMM multiplexers to input data to Compaq 386 16 MHz computers. The measuring circuits were maintained open except during the actual sampling periods (voltage measurements were allowed to stabilize for 2s before sampling and thermistor resistances were allowed to stabilize for 8s before sampling). Data were displayed in real time as well as being written to disks. An example of a set of temperature-time plots and the associated cell potential-time plots is illustrated for one experiment at three different times in Figs. 4A-C.

Experiments were carried out on 0.1, 0.2, 0.4, and 0.8 cm diameter x 10 cm long Pd (special grade, Johnson Matthey) electrodes and on 0.1 x 10 cm Pt (Johnson Matthey) electrodes. At the highest current densities used the electrode lengths were reduced to 1.25 cm and the spacing of the anode winding was also reduced. These shorter electrodes were placed in the bottom of the Dewar cells so as to ensure adequate mixing. Measurements reported here were made in D_2O (Cambridge Isotopes) of 99.9% purity; light water levels in the cells never rose above 0.5%. Results reported here have been obtained in 0.1$\underline{M}$

LiOD prepared by adding Li metal (A.D. Mackay $^6Li/^7Li$ - 1/9) to D_2O; 0.1M LiOD + 0.1M Li_2SO_4 and 1M Li_2SO_4 were prepared by adding dried Li_2SO_4 (Aldrich 99.99% anhydrous, $^6Li/^7Li$ - 1/11) to 0.1M LiOD and D_2O respectively. A single batch of electrolyte was used for any given experimental series. Blank experiments were carried out both in 0.1M LiOD in D_2O and 0.1M LiOH in H_2O.

The current efficiencies for the electrolyses according to reaction (vii) were determined by measuring the combined rates of gas evolution from the cells. Surprisingly, these efficiencies were higher than 99% as was also shown by the record of D_2O additions for experiments having low cell temperatures. Such high current efficiencies have now also been reported in other work(12,13); they can be understood in terms of the inhibition of D_2 oxidation at the anode by Pt-oxide formation and the extensive degassing of the oxygen content of the electrolyte in the cathode region by the vigorous D_2 evolution. In supersaturated, highly stirred solutions (high current densities), rapid degassing is observed even near the anode. These high current efficiencies greatly simplify the analyses of the experimental data.

Data evaluation, error analysis, and results

The "black box" representation of the calorimeters

In common with all other physicochemical and engineering devices, the evaluation of data from the behavior of the Dewar-type electrochemical calorimeters requires the construction of accurate "black-box" models, Fig. 5. In this particular case the models must account for the enthalpy and mass balances in the cell which can be combined through the current efficiency, γ, of the electrolysis. The nature of the enthalpy flows into and out of the "black box" will be apparent and we make the following additional comments:

a) the enthalpy flow into the cell due to the electrical input is $(E_{cell}(t) - \gamma E_{thermoneutral,cell})I$. The term $E_{thermoneutral,cell}$ is the cell voltage at which the electrolysis is thermoneutral; this differs from the reversible potential of reaction (vii) since the electrolysis takes place with an increase of entropy.

b) the current efficiency, γ, can be taken as unity (see above). This greatly simplifies the analysis of the data.

c) in the analysis of the data we have neglected the enthalpy content of the gas stream due to the D_2O content, $0.75\left(\frac{P}{P^* - P}\right)C_{P,D_2O,v}\,\Delta\theta$, as well as that due to the evaporation of D_2O, $0.75\left(\frac{P}{P^* - P}\right)L$. Both these terms have been written assuming the gas stream is saturated with D_2O at the relevant cell temperature. The neglect of these terms causes an underestimate of the excess enthalpy and we have throughout adopted this strategy (see further below). The terms are relatively small for values of $\Delta\theta < 20^\circ$ but the second, especially, becomes large and the dominant form of heat transfer from the cell as the temperature approaches the boiling point. Our calorimeters are unsuitable for measuring the heat outputs from the cells under these conditions.

d) heat transfer from the calorimeter to the surroundings can be written in a variety of ways depending on its design and properties as well as the chosen level of approximation$^{(11)}$. For the Dewar-type cells, Fig. 2, heat transfer for a hypothetical steady state generation of Q watts is controlled by a mixture of radiation and conduction

$$Q = k_R \left[\left(\theta_{bath} + \Delta\theta \right)^4 - \theta_{bath}^4 \right] + k_C \Delta\theta \qquad (7)$$

Similarly for the steady state following the additional injection of ΔQ watts to calibrate the system we have

$$Q + \Delta Q = k_R \left[\left(\theta_{bath} + \Delta\theta + \Delta\Delta\theta \right)^4 - \theta_{bath}^4 \right] + k_C \left[\Delta\theta + \Delta\Delta\theta \right] \qquad (8)$$

The separate determination of k_R and k_C leads to an increase in the random errors in the estimation of the heat flows from the cells. We have therefore adopted the strategy of neglecting the conductive term while making an appropriate increase in the radiative term

$$Q \cong k_R' \left[\left(\theta_{bath} + \Delta\theta \right)^4 - \theta_{bath}^4 \right] \qquad (9)$$

and

$$Q \cong k_R' \left[\left(\theta_{bath} + \Delta\theta + \Delta\Delta\theta \right)^4 - \left(\theta_{bath} + \Delta\theta \right)^4 \right] \qquad (10)$$

We have shown elsewhere$^{(11)}$ that this leads to a small systematic underestimate of the heat flow from the cell (and hence the excess enthalpy). However, as the correct value of the radiative term can be estimated from the Stefan-Boltzmann constant and the surface areas of the cells, a correction can readily applied (if this is desired) to give the heat output from the cells to within 1% of the enthalpy input or 1 milliwatt whichever is the greater. These are the figures which we have always quoted in lectures describing our initial results$^{(6,7)}$.

An important aspect of the approximations (9) and (10) is that any other term linear in $\Delta\theta$ can similarly be accounted for by making an appropriate increase or decrease in k_R (see below).

A further factor which needs to be taken into account is that for a continuously reacting chemical system (open system) such as the electrochemical Dewar cells, the cell contents change with time. The extent of the radiant surface decreases with time while the length of any parallel conduction path increases with time. To a first approximation we would therefore expect the heat transfer coefficients to decrease linearly with time and we write

$$Q \cong k_R'^0 \left[1 - \frac{(1+\lambda)\,\gamma I t}{2FM^0}\right]\left[\left(\theta_{bath} + \Delta\theta\right)^4 - \theta_{bath}^4\right] \qquad (11)$$

where the term λ allows for a more rapid decrease of the radiant surface area (and increase of the length of the conduction path) than would be predicted by electrolysis alone in view of the internal solid cell components. The superscript ^{0} here and elsewhere in this text denotes a value at a chosen time origin.

e) a general expression for the water equivalent is

$$M = M^0 - \frac{(1+\beta)\,\gamma I t}{2F} \qquad (12)$$

where, as for the heat transfer coefficient, the term β allows for a more rapid decrease of the water equivalent with time than would be predicted by electrolysis alone.

f) the term $\frac{\gamma I}{F}\int_0^t \left[0.5 + 0.75\left(\frac{P}{P^* - P}\right)\right] C_{P,D_2O,\ell}\,\Delta\theta'\,dt$ is the enthalpy input to the cell due to the addition of D_2O to make up for the losses due to electrolysis and evaporation. Here $\Delta\theta'$ is the difference in temperature between the cell and make-up stream. In practice it has been found convenient to add D_2O at fixed intervals of time and, provided measurements are initiated at times longer than 6 thermal relaxation times following this addition, the effect of this term can be neglected in the further analysis.

We therefore obtain the differential equation governing the behavior of the calorimeter

$$C_{P,D_2O,\ell}\left[M^0 - \frac{(1+\beta)\,\gamma It}{2F}\right]\frac{d\Delta\theta}{dt} - C_{P,D_2O,\ell}\,\frac{(1+\beta)\,\gamma I\Delta\theta}{2F}$$

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

$$- \frac{\gamma I}{F}\left\{\left[0.5C_{P,D_2} + 0.25C_{P,O_2} + 0.75\left(\frac{P}{P^* - P}\right)C_{P,D_2O,v}\right]\Delta\theta + 0.75\left(\frac{P}{P^* - P}\right)L\right\}$$

$$- k_R'^0\left[1 - \frac{(1+\lambda)It}{2FM^0}\right]\left[\left(\theta_{bath} + \Delta\theta\right)^4 - \theta_{bath}^4\right] \qquad (13)$$

Equation (13) is difficult to apply because $E_{cell}(t)$ and $Q_f(t)$ are unknown functions of time. We note, however, that since we are only concerned with small changes of temperature at any given origin, θ^0, we can carry out a Taylor series expansion at this point and, retaining only the first derivatives we obtain

$$\left\{\frac{dE_{cell}}{d\theta} + \frac{d}{d\theta}\left[\frac{0.75I}{F}\left(\frac{P}{P^* - P}\right)\left(C_{P,D_2O,v}\,\Delta\theta + L\right)\right]\right\}I\Delta\theta' = \frac{\psi I}{\theta^0}\,\Delta\theta' \qquad (14)$$

We assume also that Q(t) is constant during any one measurement cycle and, taking note also of

$$\Delta H^{\emptyset}_{cell} = \Delta H^{\emptyset}_{bath} + \sum_i \nu_i C_{P,i}\Delta\theta \qquad (15)$$

as well as of b) and c) we can write (13) in the more tractable form

$$
\begin{aligned}
& C_{P,D_2O,\ell}\left[M^0-\frac{(1+\beta)It}{2F}\right]\frac{d\Delta\theta}{dt}-C_{P,D_2O,\ell}\;\frac{\beta I\Delta\theta}{2F} \\
&= \left(E^0_{cell}-E_{thermoneutral,bath}+\frac{\psi\Delta\theta'}{\theta^0}\right)I+Q_f(t)+\Delta QH(t-t_1)-\Delta QH(t-t_2) \\
&- k_R^{\prime 0}\left[1-\frac{(1+\lambda)It}{2FM^0}\right]\left[\left(\theta_{bath}+\Delta\theta\right)^4-\theta_{bath}^4\right] \qquad (16)
\end{aligned}
$$

Data Evaluation and Error Analysis

Analytical solutions using the linearization of the radiative heat transfer term show that the heat transfer coefficient to be used in the evaluation of Q_f from measurements at a single point is $\left(k_R'^0 - \frac{\psi I}{\theta^0}\right)\left[1 - \frac{(1 + \lambda)It}{2FM^0}\right]$. This result would in fact also be predicted directly by applying the argument outlined in d) of the previous section to Equation (16) but would not be predicted from elementary considerations of the heat balance at a single operating point. The result highlights the need to fit the whole of the experimental $\Delta\theta$-t plot to Equation (16) in accurate evaluations of Q_f.

The analytical solutions give results which are in close accord with the experimental data for small values of $\Delta\theta$ (these solutions will naturally not be applicable for large values of $\Delta\theta$ say, $>10^\circ C^{(11)}$). In order to obtain approximate values of Q, $k_R'^0\left[1 - \frac{(1 + \lambda)It}{2FM^0}\right]$, and Q_f we have therefore applied the calculation scheme illustrated in Fig. 6 using equations (9) and (10). Calibrations in which an amount of heat, Q, is injected into the cell using the resistive heater, have shown that this can be accurately recovered by injecting a further amount ΔQ and by applying (9) and (10). Nevertheless the estimates of Q and Q_f based on the approach using the scheme outlined in Fig. 6 are evidently approximate, Tables 1 and 2. Accurate values of Q have therefore been obtained by fitting the whole of the transient calculated from (16) to the experimental data using non-linear regression. In this fitting procedure we have used the simplest forward integration method

$$\Delta\theta_{n+1} = \Delta\theta_n + \left(\frac{d\Delta\theta}{dt}\right)_n \Delta t \qquad (17)$$

and we have used the parameters Q, $k_R'^0$, Q_f and $(1 + \lambda)$ estimated according to Fig. 6 as starting values for the regression procedures. The parameter ψ has been estimated from the E_{cell}- t plot using linear regression; in this way the number of parameters to be fitted to (16) has been reduced from 5 to 4 thereby speeding the calculation. In view of the curvature of the parameter space hypersurfaces, it has also been found to be convenient to regard $\dfrac{\left(E^0_{cell} - E_{thermoneutral,bath}\right)I + Q_f}{C_{P,D_2O,\ell} M^0}$ as one of the free parameters of the calculation.

We have used a Marquardt-type algorithm for the fitting procedure and it should be noted that the diagonal elements of the error matrix derived in this calculation (the inverse of the matrix used in the parameter estimation) directly give the standard deviation of the parameters. In this way we have shown that the parameter $\dfrac{\left(E^0_{cell} - E_{thermoneutral,bath}\right)I + Q_f}{C_{P,D_2O,\ell} M^0}$ can be estimated to 0.1% throughout the operating range. This is also the error of $\left(E^0_{cell} - E_{thermoneutral,bath}\right)I + Q_f$ since the error of M^0 is ≅ 0.01%. Even higher precisions could well be achieved by using more structured $\Delta\theta$ - t profiles than those of Figs. 6 and 7 but we have not done this so far in our work as we have only estimated $\left(E^0_{cell} - E_{thermoneutral,bath}\right)I$ to ≅ 0.1% (the error of this quantity is controlled by σ_I). This error must be added to that of $\left(E^0_{cell} - E_{thermoneutral,bath}\right)I + Q_f$ to obtain the total error of the excess enthalpy listed in Tables 1 and 2.

Results

Fig. 7 illustrates the degree of fit which can be obtained by using the non-linear regression procedure outlined in the previous section and Tables 1 and 2 illustrate the results of measurements of the excess enthalpy using both the approximate and exact methods of data analysis. We have also included some data taken prior to our first publication (6,7) which were obtained using only the approximate method of data analysis.

The marked excess enthalpy production on 0.1 and 0.2 and 0.4 cm diameter electrodes, (Table 1) must be viewed in terms of the slightly negative excess enthalpies for the blank experiments, Table 2.[1] This slightly negative value is due to the method of calculation which underestimates the heat output from the cell (see previous section). In many ways we regard the "zero" result on 0.8 cm diameter electrodes (and on the sheet electrode at low current density) as the most significant blank as it shows that almost exact thermal balances can be obtained using our methodology for systems identical to those giving marked excess enthalpy. The differences between the 0.1, 0.2, 0.4 and the 0.8 cm electrodes also point to the importance of the metallurgical procedures in devising electrodes showing excess enthalpy generation.

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[1] Much of this data was available at the time of our first publication but the Editor of Nature refused to publish a letter to correct the many erroneous statements which had been made in the Editorials of the Journal.

Discussion

It can be seen that many (perhaps all?) of the assertions e.g.(14-21) which have been made about our experiments are erroneous. We would stress here that it is perfectly possible to obtain accurate values of the heat output from the cells and, hence, the excess enthalpy provided due attention is paid to the design of the calorimeters and control of the environment and providing modern methods of data analysis are used. We would also stress the importance of deriving error estimates from a single experiment rather than from the variation of a parameter (here the excess enthalpy) from a set of experiments as the variability of the parameter may itself be a key feature of the phenomenon to be observed. In this context it is of interest that the variability of the results at low to intermediate current densities (which have been widely used in attempts to replicate our work) is large and far in excess of the errors of each individual experiment. This variability may point to the importance of the precise nature of the surface conditions and/or history of the electrodes in defining the phenomenon.

It can be seen that the excess enthalpies increase markedly with the current density so much so that the results have the appearance of a threshold phenomenon. However, experiments of very high precision at low current densities are required before this can be confirmed. On balance we still believe that the results confirm that excess heat generation is a bulk phenomenon, Fig. 8, although this cannot now be stated as firmly as it appeared from the results available in the spring of 1989. The levels of enthalpy generation during the duration of a typical experiment (3 months) are such (hundreds of Megajoules cm^{-3}) that they must be attributed to nuclear processes. In particular, it is inconceivable that chemical or non-nuclear physical energy could be stored in the system at these levels and then be released over prolonged periods of time(22). The phenomenon of "bursts" in the enthalpy production which we first described(23) shortly after the publication of our preliminary paper(6) is also of interest in this context. Figs. 9A, B and C illustrate the $\Delta\theta$ - t , the specific excess enthalpy - t and the cumulative specific enthalpy - t data for the largest "burst" we have observed to date. The total specific excess over the period of the "burst" ($\cong$16 MJ cm^{-3} over 16 days) is again of such a magnitude that the heat release can only be attributed to nuclear processes. The heat output during this burst was 17 times (average value) and 40 times (peak value) of the enthalpy input. In some cells e.g. Fig. 10, the temperature rises rapidly to boiling. When this occurs, it is difficult to accurately measure the heat flows (see section c above). The heat output, however, must be extremely high.

We have confined attention to the calorimetric data but here note finally that it is perfectly feasible to observe very low levels of neutron production (of the order 10^{-3} - $10^{-2}s^{-1}$) from cells generating excess heat providing counting is extended over prolonged periods of time(24); tritium production up to a level 8 times the starting concentration has been observed in experiments in Utah following "bursts" in the enthalpy production(25). It is hardly possible to attribute such observations to the operation of a set of non-nuclear phenomena. Providing adequate funding is available, an high priority for further work must be the identification of the products of these nuclear reactions. Our current work is concentrated on the design and implementation of factorial experiments in which we are seeking to define more closely the effects of the many variables which control the excess enthalpy. The instrumentation and procedures which we are using in the execution of these experiments are essentially the same as those described in this paper.

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Table 1. Excess enthalpy observed for 0.1, 0.2, and 0.4 cm diameter palladium rods as a function of current density, time elapsed since start of experiment, electrolyte composition, and electrode batch.

Rod Dia.	Batch[a] & Electrolyte[b]		Current Density	E_{cell}	Q_{input}	Q_{excess}	Approximate Specific Q_{excess}	Specific Q_{excess} From Regression Analysis	
/cm			/mA cm^{-2}	/V	/W	/W	/W cm^{-3}	/W cm^{-3}	
0.1	1	𝒟 ○	8	2.754	0.0304	0.0075	0.095		
0.1^{c}	1	𝒟 ○	64	3.637	0.419	0.042	0.53		
0.1*	3	𝒮 ◑	64	2.811	0.032	0.001	0.140	0.1442	±0.0002
0.1	2	𝒟 ○	128	4.000	0.984	0.160	2.04	2.043	±0.003
0.1*	3	𝒮 ◑	128	3.325	0.089	0.005	0.486	0.5131	±0.0006
0.1	2	𝒟 ○	256	5.201	2.93	0.313	3.99	4.078	±0.007
0.1^{*c}	1	𝒟 ○	512	9.08	1.51	0.17	17.3		
0.1	2	𝒟 ○	512	6.085	7.27	1.05	13.4	13.77	±0.02
0.1*	3	𝒟 ○	1024	11.640	4.04	1.03	105.	112.8	±0.1
0.2	1	𝒟 □	8	2.702	0.058	0.036	0.115		
0.2^{c}	1	𝒟 □	64	4.139	1.040	0.123	0.39		
0.2	3	𝒮 ◨	64	4.780	1.30	0.006	0.019	0.021	±0.001
0.2	3	ℳ ◧	64	3.930	0.956	0.024	0.077	0.077	±0.001
0.2	3	𝒟 □	128	8.438	5.52	1.65	5.25	5.68	±0.01
0.2*	3	𝒮 ◨	128	4.044	0.250	0.028	0.713	0.714	±0.001
0.2*	3	ℳ ◧	256	6.032	0.898	0.056	1.42	1.498	±0.002
0.2^{*c}	1	𝒟 □	512	8.25	2.68	0.66	16.8		
0.2*	3	ℳ ◧	512	9.042	3.00	0.603	15.3	16.03	±0.01
0.2*	3	𝒮 ◨	1024	7.953	5.13	2.80	71.2	75.42	±0.08
0.4	1	𝒟 △	8	2.910	0.137	0.153	0.122		
0.4^{c}	1	𝒟 △	64	5.137	2.88	0.502	0.40		
0.4	2	𝒟 △	64	5.419	3.10	0.263	0.209	0.214	±0.003
0.4**	2	𝒟 △	64	4.745	2.24	0.117	0.106	0.145	±0.002
0.4*	2	ℳ ◭	64	3.519	0.198	0.0005	0.002	0.0023	±0.0002
0.4	2	𝒟 △	128	6.852	8.50	1.05	0.84	0.842	±0.009
0.4*	2	𝒟 △	256	7.502	2.38	0.311	1.98	1.999	±0.003
0.4^{*c}	1	𝒟 △	512	8.66	5.70	2.18	13.9		
0.4*	2	𝒟 △	512	10.580	7.23	1.65	10.5	11.09	±0.02

(a) All rod lengths 10cm or *1.25cm or **8.75cm

(b) 𝒟: 0.1M LiOD; 𝒮: 0.50M Li2SO4; ℳ: 0.1M LiOD + 0.45M Li2SO4. All measurements were made in the same batch of D_2O of 99.9% isotopic purity. All measurements in 𝒮 or ℳ have been made since March,1989.

(c) Measurements made prior to March, 1989; different data set to that shown in the preliminary paper(6,7).

Table 2. Results for blank experiments on platinum and palladium rods as a function of current density, time elapsed since start of experiment, and electrolyte composition.

Rod Dia.[a]	Batch[a] & Electrolyte[c]	Current Density	E_{cell}	Q_{input}	Q_{excess}	Approximate Specific Q_{excess}	Specific Q_{excess} From Regression Analysis
/cm		/mA cm^{-2}	/V	/W	/W	/W cm^{-3}	/W cm^{-3}
Palladium Electrodes:							
0.1	2 W	32	3.605	0.212	-0.001	-0.009	-0.0097 ±0.0002
0.1	2 W	64	3.873	0.479	-0.001	-0.014	-0.0165 ±0.0005
0.1	2 W	128	5.186	1.482	-0.001	-0.001	-0.001 ±0.001
0.1	2 W	256	8.894	5.931	-0.001	-0.007	-0.008 ±0.006
0.1	2 W	512	11.29	15.70	-0.001	-0.008	-0.01 ±0.02
[b]	D	0.8	2.604	1.458	-0.001	-0.000	
0.8	1 D	8	3.365	0.365	-0.001	-0.000	-0.001 ±0.004
0.8	2 D	8	3.527	0.397	-0.003	-0.000	-0.0006 ±0.0003
Platinum Electrodes:							
0.1	D	64	3.800	0.452	0.000	0.000	-0.0007 ±0.0004
0.1	D	64	4.138	0.520	-0.001	-0.008	-0.0094 ±0.0005
0.1	D	256	6.218	3.742	-0.001	-0.028	-0.032 ±0.004
0.1	W	64	4.602	0.624	-0.002	-0.023	-0.0232 ±0.0006
0.1	W	64	4.821	0.668	-0.003	-0.038	-0.0392 ±0.0006
0.1	W	512	12.02	16.86	-0.001	-0.007	-0.01 ±0.02

(a) All rod lengths 10cm.

(b) Palladium sheet electrode 8 x 8 x 0.2cm.

(c) D: 0.1M LiOD; W: 0.1M LiOH; All measurements in D_2O were made in the same batch as that used in the experiments in Table 3.

GLOSSARY OF SYMBOLS USED

$C_{P,D_2O,\ell}$	Heat capacity of liquid D_2O, J mol^{-1}.
$C_{P,D_2O,v}$	Heat capacity of D_2O vapor, J mol^{-1}.
$C_{P,i}$	Heat capacity of O_2, D_2, or $(D_2O)_\ell$, J 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}.
H	Heaviside unity function.
I	Cell current, A.
k_C	Heat transfer coefficient due to conduction, W·K^{-1}.
k_R	Heat transfer coefficient due to radiation, W K^{-4}.
k_R^0	Heat transfer coefficient due to radiation at a chosen time origin.
k_R'	Effective heat transfer coefficient due to radiation, W K^{-4}.
$k_R'^0$	Effective heat transfer coefficient due to radiation at a chosen time origin, W K^{-4}.
ℓ	Symbol for liquid phase.
L	Enthalpy of evaporation, J mol^{-1}.
M	Heavy water equivalent of the calorimeter, mols.
M^0	Heavy water equivalent of the calorimeter at a chosen time origin.
n	Iteration number (data point number).
P	Partial pressure, Pa.
P	Fugacity, Pa.
P*	Atmospheric pressure, Pa.

Q	Rate of steady state heat generation at a given temperature, W.
Q_f	Rate of generation of excess enthalpy, W.
R	Gas constant, 8.31441 J $K^{-1}mol^{-1}$.
T	Absolute temperature, K.
t	Time, s.
β	Dimensionless term allowing for more rapid time dependent decrease of water equivalent of cell than that expected from electrolysis alone.
γ	Current efficiency of electrolysis toward a given reaction.
ΔH^{0}	Standard free enthalpy change, J mol^{-1}.
ΔQ	Rate of heat dissipation of calibration heater, W.
$\Delta\theta$	Difference in cell and bath temperature at a given rate of enthalpy release, K.
$\Delta\theta'$	$\Delta\theta - \Delta\theta^{0}$, K.
$\Delta\theta^{0}$	Cell temperature at a chosen time origin, K.
$\Delta\theta_{n}$	Difference in cell and bath temperature at the n^{th} time interval, K.
$\Delta\theta_{n,calc}$	Calculated difference in cell and bath temperature at the n^{th} time interval, K.
$\Delta\theta_{n,exp}$	Difference in experimental cell and bath temperature at the n^{th} time interval, K.
$\Delta\Delta\theta$	Temperature rise in cell due to application of a calibration pulse of heat, K.
θ_{bath}	Bath temperature, K.
λ	Dimensionless term allowing for more rapid time dependent decrease of heat transfer coefficient of cell than that expected from electrolysis alone.
$\bar{\mu}_{i}^{0}$	Standard state electrochemical potentials, J.
$\bar{\mu}_{i}$	Electrochemical potentials, J.

ν_i	Stoichiometric coefficients.
σ_n	Sample standard deviation of a given temperature measurement, K.
χ^2	Sum of inverse variance weighted deviations between experimental data and values predicted by the model using the non-linear regression fitting algorithm.
ϕ_m	Galvani potential in the metal, V.
ϕ_s	Galvani potential in the solution, V.
ψ	Slope of the change of cell potential with temperature, V.

Figure Legends

1. Schematic diagram of the D_2O-Pd interface, indicating the pertinent reactions at the cathode and approximate energetics of the interfacial region and of the Pd lattice. $\phi_m - \phi_s$ is the galvani potential difference across the interface.

2. The single compartment Dewar calorimeter electrolysis cell used in this work.

3. Schematic diagram of the feedback circuit used in this work for conversion of a potentiostat to a galvanostat with effective protection against electrical oscillation.

4A. Temperature above bath vs. time and cell potential vs. time data for a 0.4 x 10 cm Pd rod in 0.1M LiOD solution. The applied current was 800 mA, the bath temperature was 29.87 °C, and the estimated Q_f was 0.158 W. The time of the measurement (taken at the end of the calibration pulse) was at approximately 0.45×10^6s after the beginning of the experiment.

4B. Same as Fig. 4A except the time of measurement was at approximately 0.89×10^6s. Estimated $Q_f = 0.178$ W.

4C. Same as Fig. 4A except the time of measurement was at approximately 1.32×10^6s. Estimated $Q_f = 0.372$ W.

5. Schematic diagram of the complete "black box" model of the Dewar calorimeter used in this work (see Fig. 2).

6. Schematic diagram of the method used for the determination of the heat flow in the Dewar cell, Fig. 2.

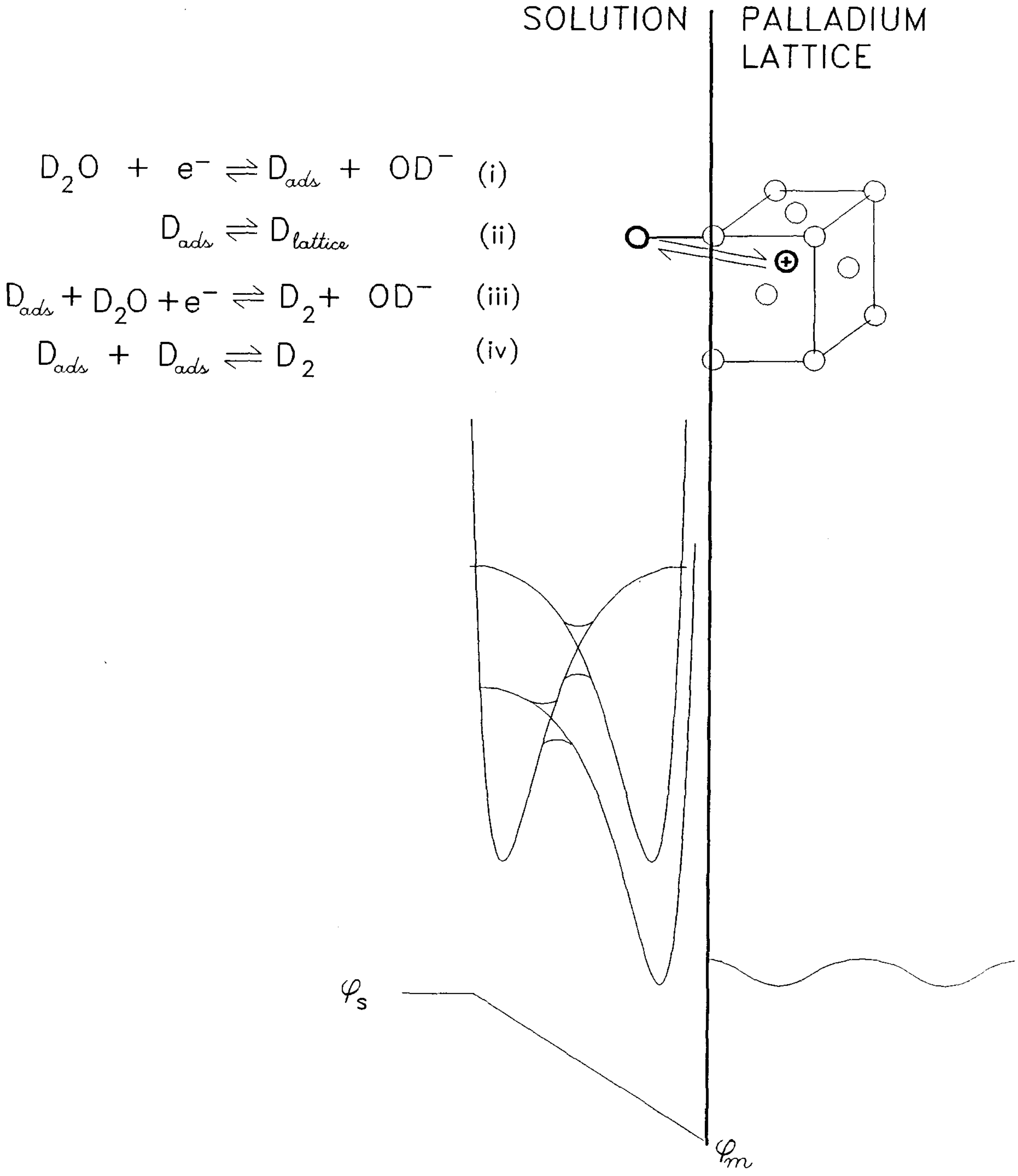
7. Figure showing the degree of fit of the "black box" model in Eqn. (10) to actual experimental data from an experiment using a 0.2 x 10cm Pd rod cathode in 0.1MLiOD. The dotted line in the figure represents the fit obtained using estimated values of the several cell parameters and was obtained by the forward integration technique described in the text to force the fit of the data to the model at the starting point ($t = 0$), the point of application of the calibration heater pulse, the point at the end of the calibration heater pulse, and the point at the end of the experiment. The solid line (which in this figure is coincident with the experimental data) is the fit obtained to the model by using the Marquardt algorithm for the non-linear regression technique described in the text.

8. Log-log plot (Excess enthalpy vs. current density) of the data in Table 1

9. A. Responses for a large, extended "burst" of excess enthalpy The figure shows the cell temperature vs. time (upper plot) and the cell potential vs. time (lower plot) for a 0.4 x 1.25 cm Pd rod electrode in 0.1M LiOD solution. The current density was 64 mA cm^{-2}, and the bath temperature was 29.87 °C.

   B. Figure showing the calculated rate of excess enthalpy generation as a function of time, and
   C. Figure showing the total specific excess energy output as a function of time for this cell.

10. Plot of cell temperature vs. time plot for a 0.4 x 1.25 cm Pd electrode in 0.1M LiOD just prior to a period during which the cell went to boiling.



SOLUTION
PALLADIUM LATTICE
φ_s
φ_m

$$D_2O + e^- \rightleftharpoons D_{ads} + OD^- \quad (i)$$

$$D_{ads} \rightleftharpoons D_{lattice} \quad (ii)$$

$$D_{ads} + D_2O + e^- \rightleftharpoons D_2 + OD^- \quad (iii)$$

$$D_{ads} + D_{ads} \rightleftharpoons D_2 \quad (iv)$$

Fig. 1.

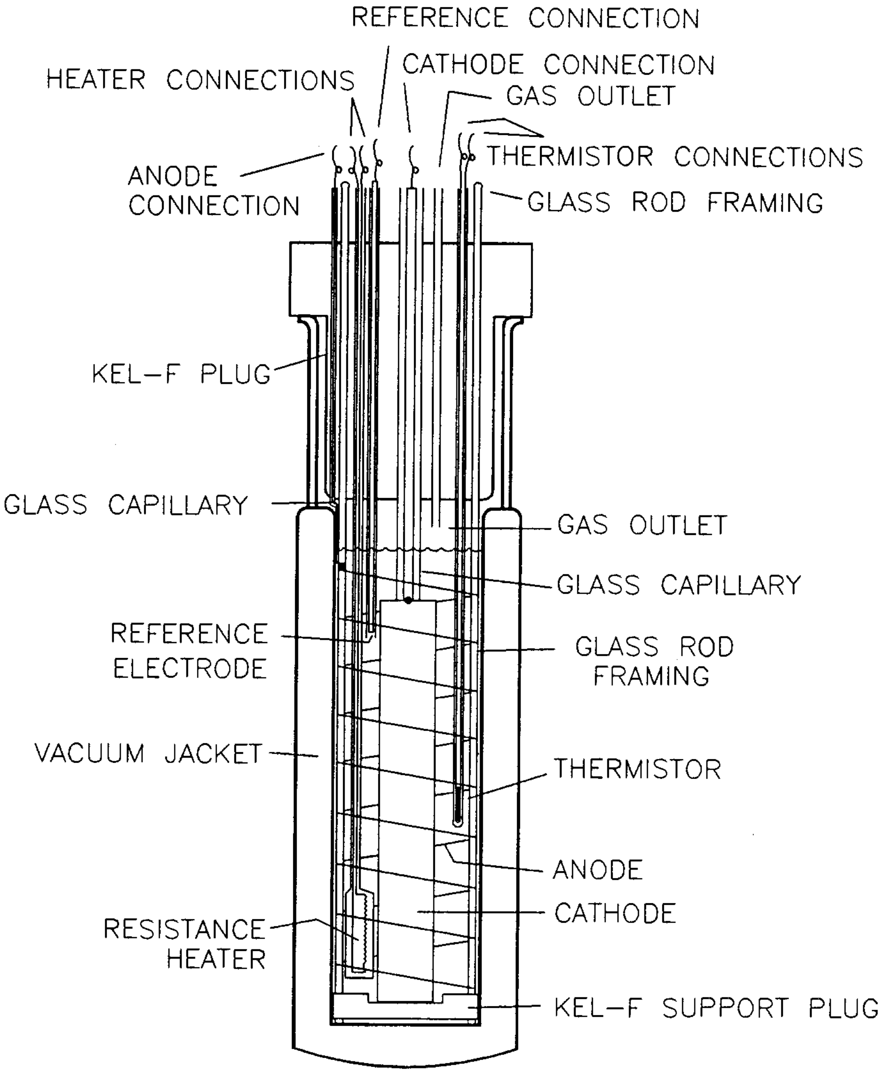
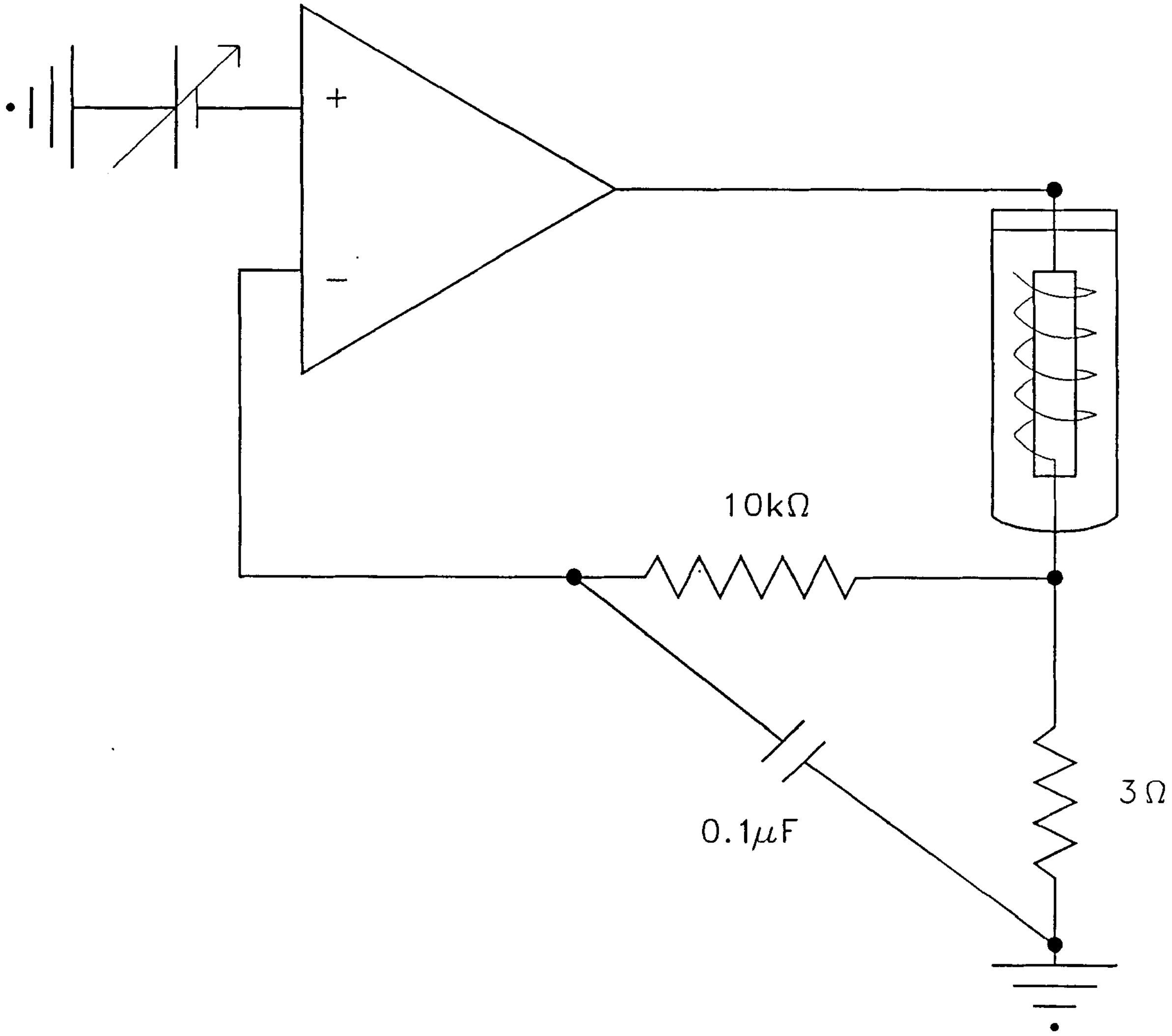

REFERENCE CONNECTION
HEATER CONNECTIONS
CATHODE CONNECTION
GAS OUTLET
THERMISTOR CONNECTIONS
ANODE CONNECTION
GLASS ROD FRAMING
KEL–F PLUG
GLASS CAPILLARY
GAS OUTLET
GLASS CAPILLARY
REFERENCE ELECTRODE
GLASS ROD FRAMING
VACUUM JACKET
THERMISTOR
ANODE
CATHODE
RESISTANCE HEATER
KEL–F SUPPORT PLUG

Fig. 2.


+
−
10kΩ
3Ω
0.1μF

SCHEMATIC OF GALVANOSTAT

Fig. 3

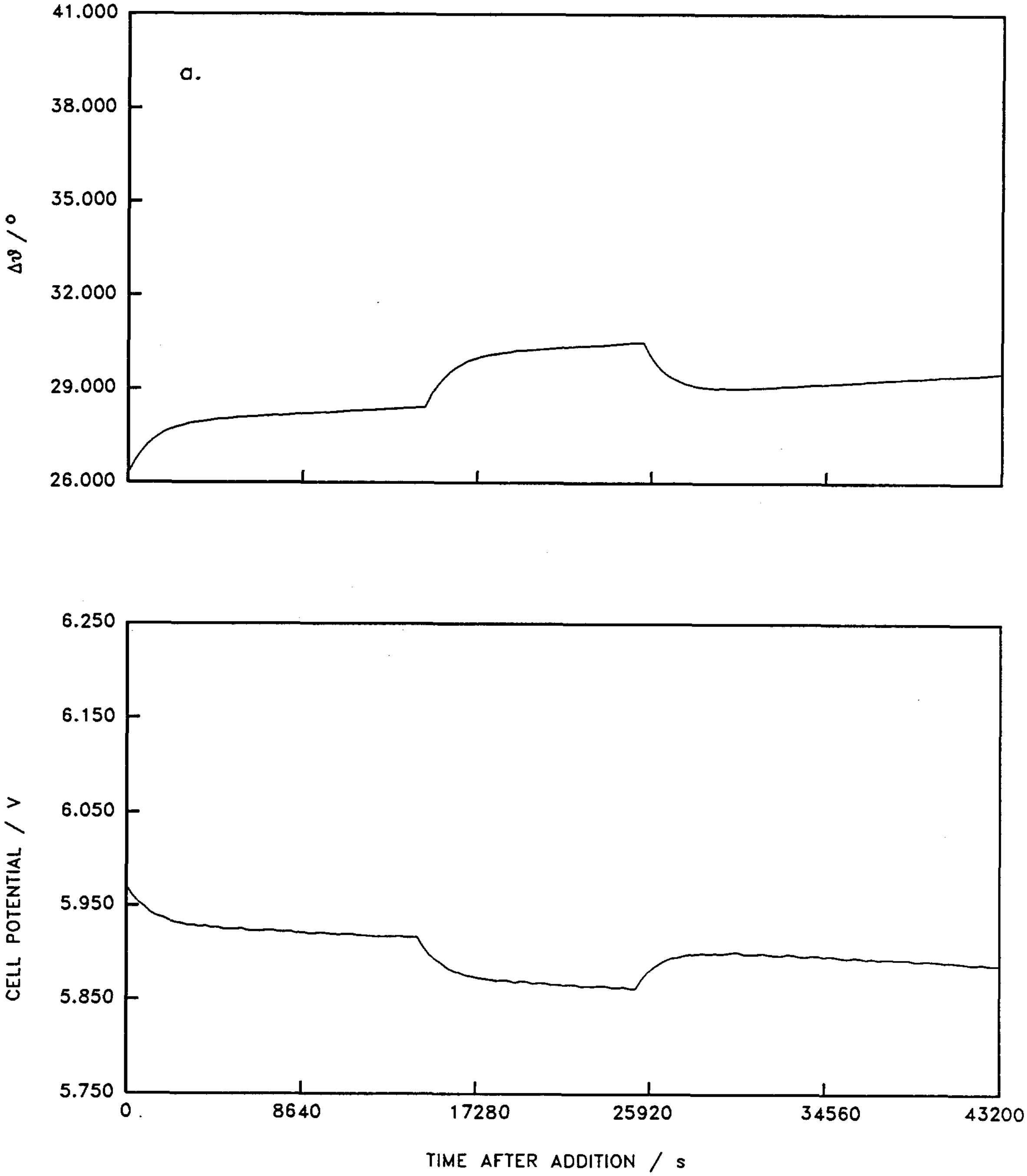

a.
41.000
38.000
35.000
32.000
29.000
26.000
Δϑ / °
6.250
6.150
6.050
5.950
5.850
5.750
CELL POTENTIAL / V
0.
8640
17280
25920
34560
43200
TIME AFTER ADDITION / s

Fig. 4a.

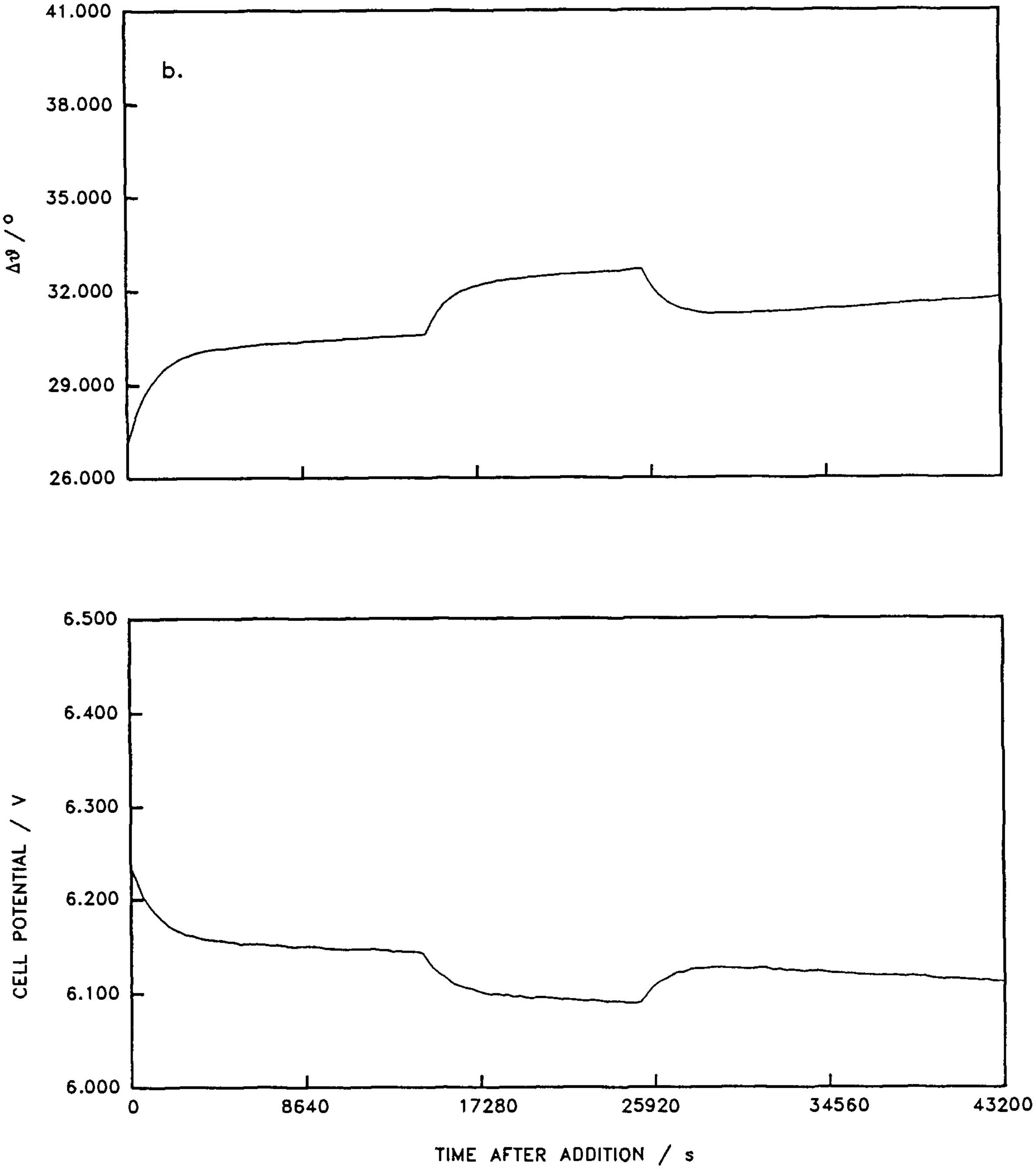

b.
41.000
38.000
35.000
32.000
29.000
26.000
Δϑ / °
6.500
6.400
6.300
6.200
6.100
6.000
CELL POTENTIAL / V
0
8640
17280
25920
34560
43200
TIME AFTER ADDITION / s

Fig. 4b.

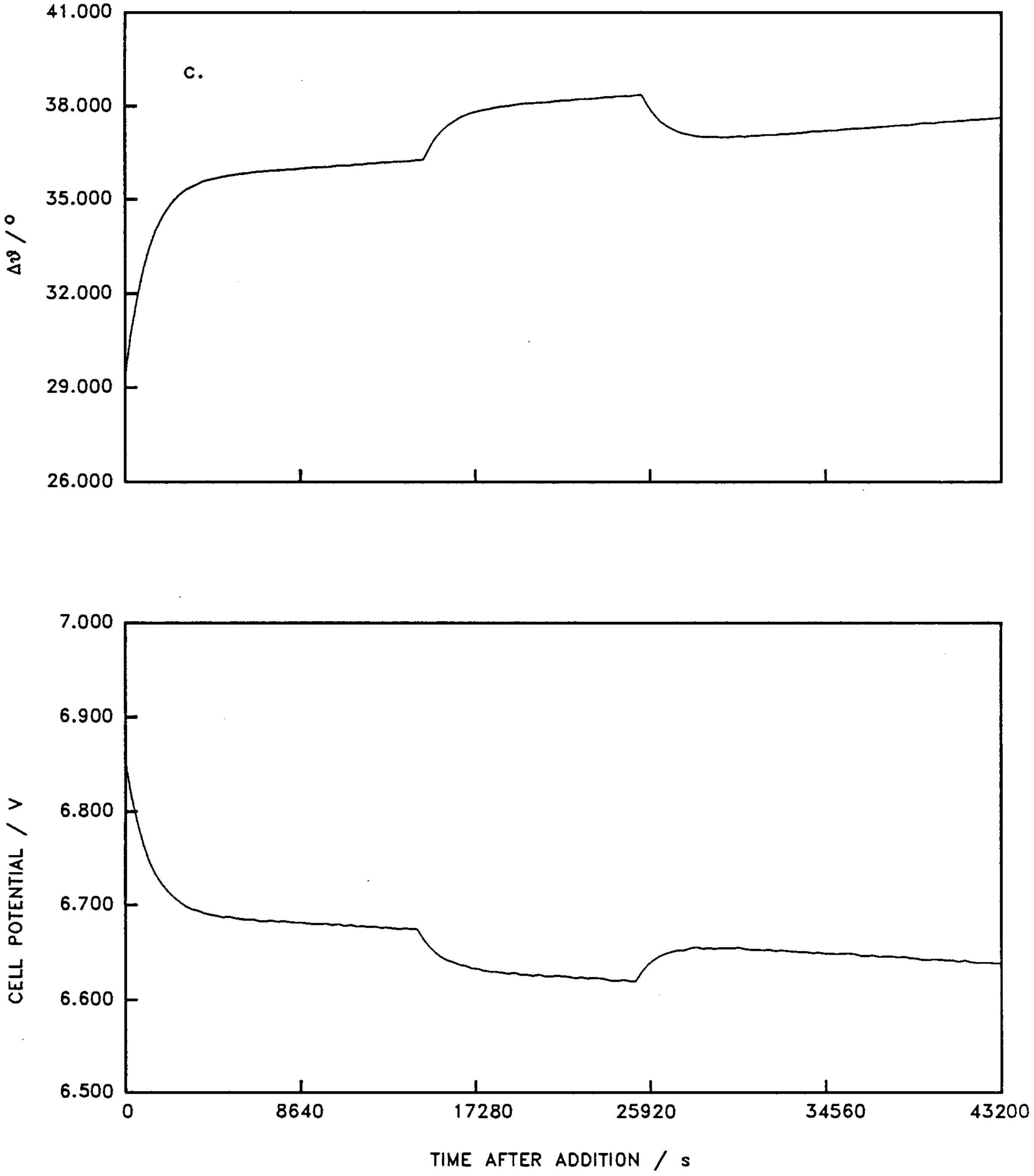

c.
41.000
38.000
35.000
32.000
29.000
26.000
Δϑ / °
7.000
6.900
6.800
6.700
6.600
6.500
CELL POTENTIAL / V
0
8640
17280
25920
34560
43200
TIME AFTER ADDITION / s

Fig. 4c.

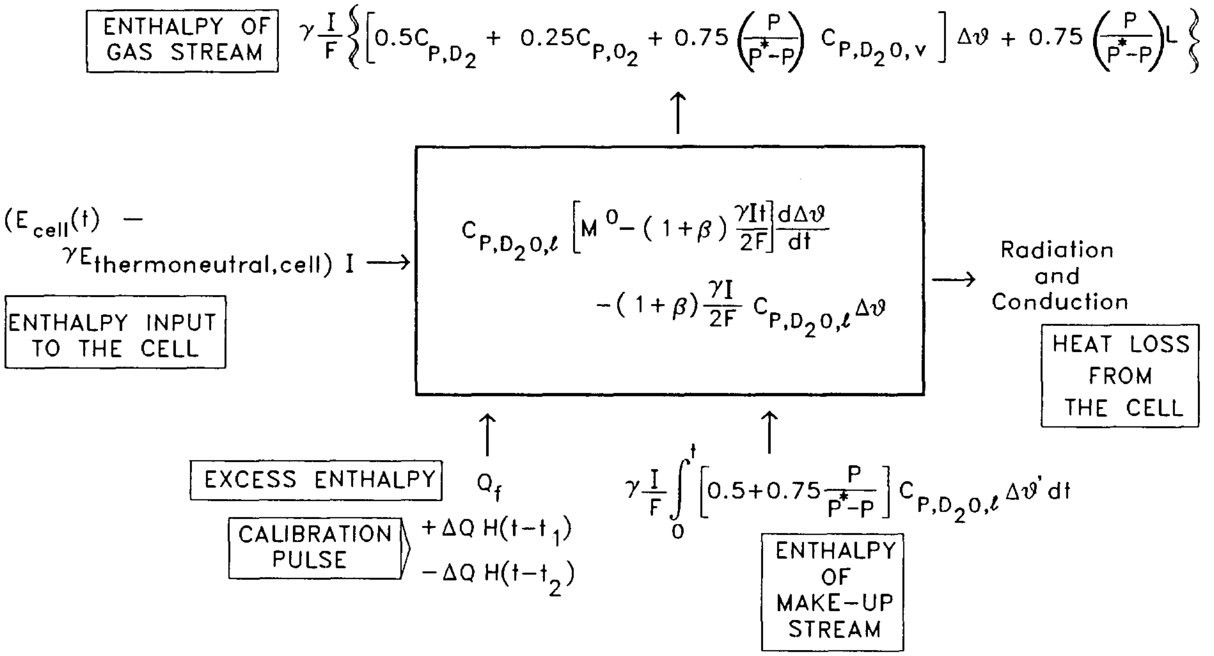

ENTHALPY OF GAS STREAM
$\gamma \frac{I}{F}\left\{\left[0.5C_{P,D_2} + 0.25C_{P,O_2} + 0.75\left(\frac{P}{P^*-P}\right) C_{P,D_2O,v}\right]\Delta\vartheta + 0.75\left(\frac{P}{P^*-P}\right)L\right\}$
$(E_{cell}(t) - \gamma E_{thermoneutral,cell})\, I$
ENTHALPY INPUT TO THE CELL
$C_{P,D_2O,\ell}\left[M^0-(1+\beta)\frac{\gamma It}{2F}\right]\frac{d\Delta\vartheta}{dt}$
$-(1+\beta)\frac{\gamma I}{2F}C_{P,D_2O,\ell}\Delta\vartheta$
Radiation and Conduction
HEAT LOSS FROM THE CELL
EXCESS ENTHALPY
Q_f
CALIBRATION PULSE
$+\Delta Q\, H(t-t_1)$
$-\Delta Q\, H(t-t_2)$
$\gamma \frac{I}{F}\int_0^t \left[0.5+0.75\frac{P}{P^*-P}\right] C_{P,D_2O,\ell}\Delta\vartheta' dt$
ENTHALPY OF MAKE-UP STREAM

Fig. 5.

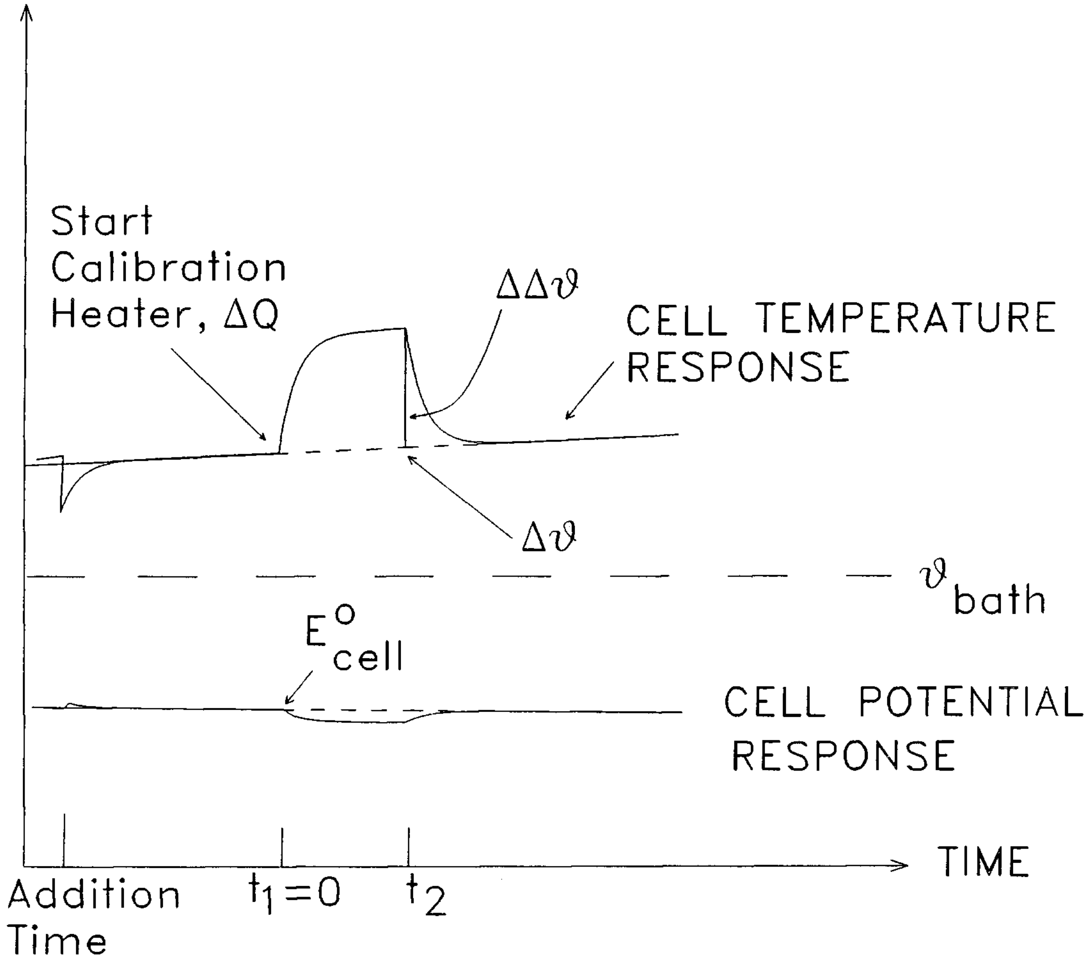

Start
Calibration
Heater, ΔQ
ΔΔϑ
CELL TEMPERATURE
RESPONSE
Δϑ
ϑ bath
E° cell
CELL POTENTIAL
RESPONSE
TIME
Addition
Time
t1=0
t2

Fig. 6.

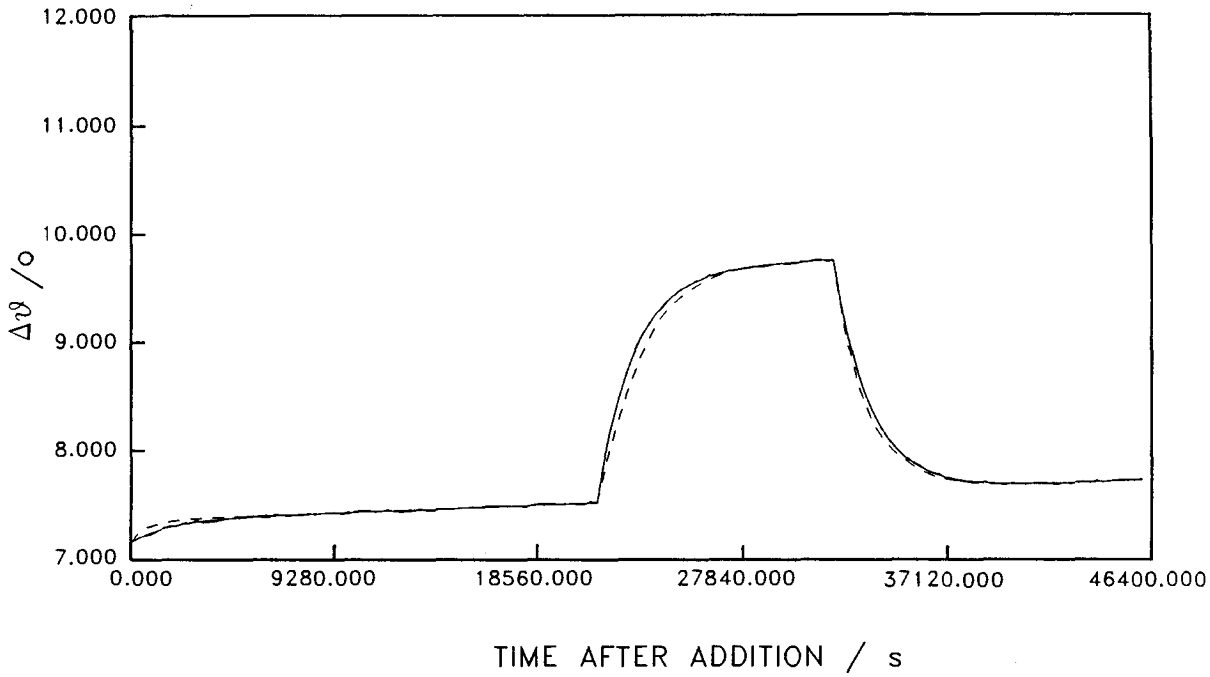

12.000
11.000
10.000
9.000
8.000
7.000
Δϑ /o
0.000
9280.000
18560.000
27840.000
37120.000
46400.000
TIME AFTER ADDITION / s

Fig. 7.

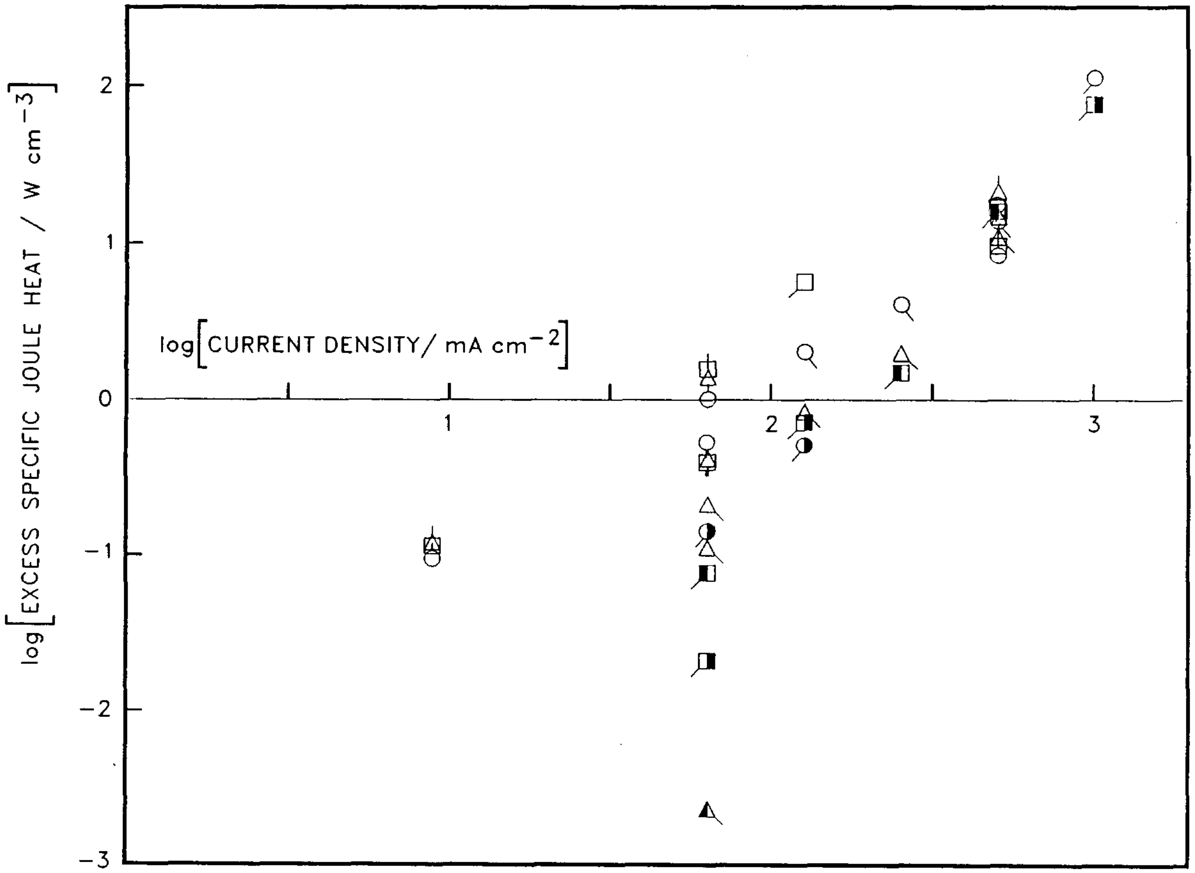

log[EXCESS SPECIFIC JOULE HEAT / W cm⁻³]
2
1
0
-1
-2
-3
log[CURRENT DENSITY/ mA cm⁻²]
1
2
3

Fig. 8.

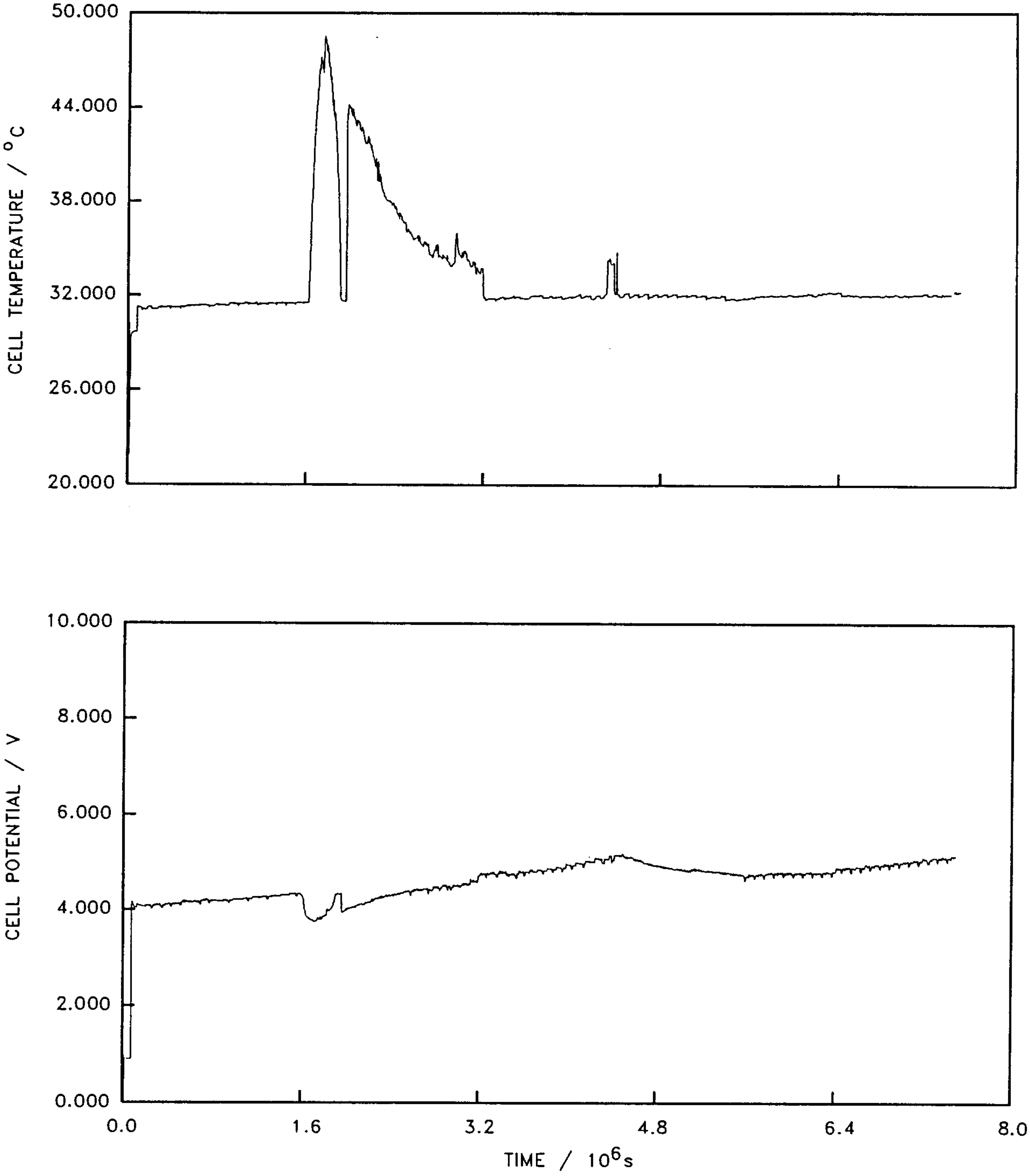

50.000
44.000
38.000
32.000
26.000
20.000
CELL TEMPERATURE / °C
10.000
8.000
6.000
4.000
2.000
0.000
CELL POTENTIAL / V
0.0
1.6
3.2
4.8
6.4
8.0
TIME / 10⁶s

Fig. 9a.

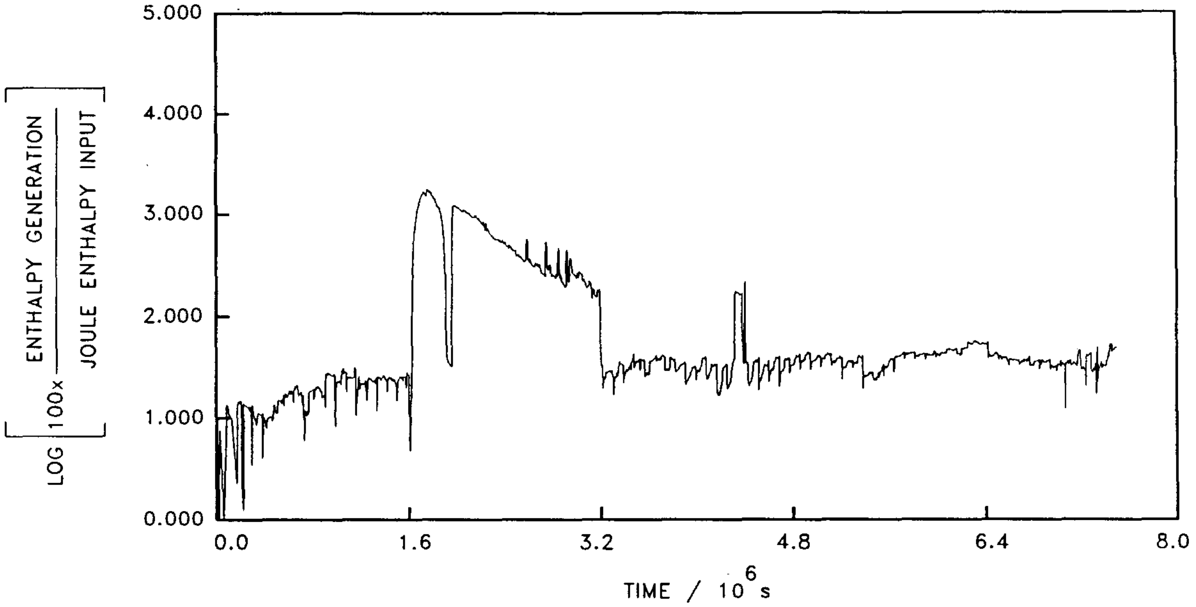

5.000
4.000
3.000
2.000
1.000
0.000
LOG [100x ENTHALPY GENERATION / JOULE ENTHALPY INPUT]
0.0
1.6
3.2
4.8
6.4
8.0
TIME / 10^6s

Fig. 9b.

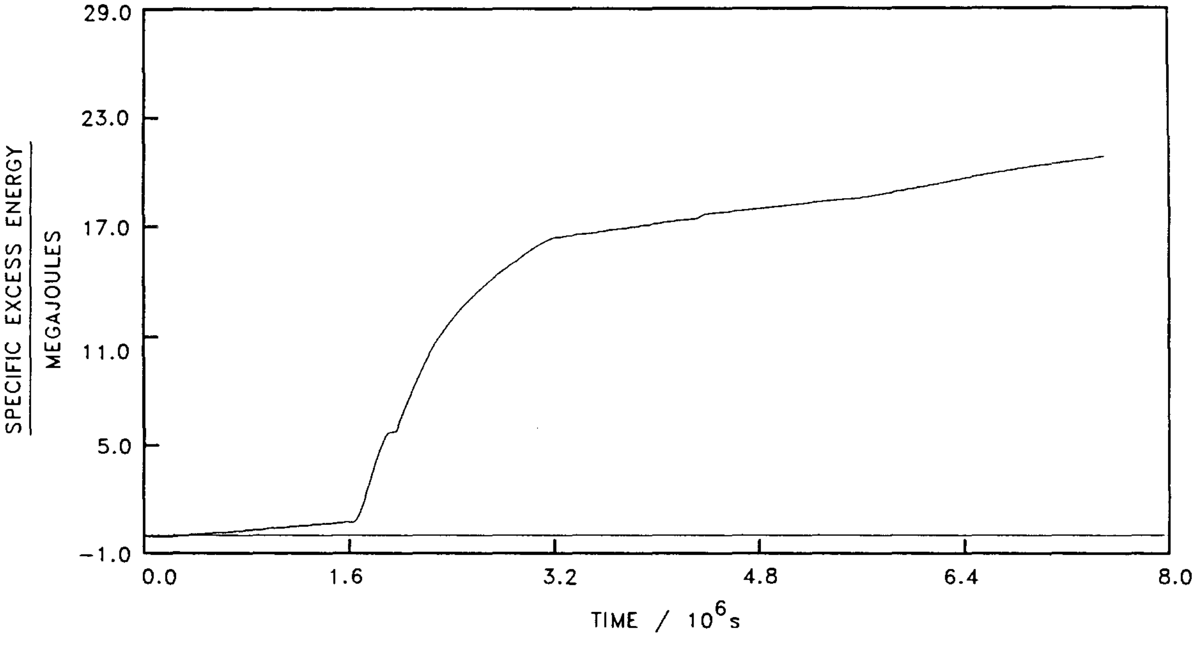

29.0
23.0
17.0
11.0
5.0
−1.0
SPECIFIC EXCESS ENERGY / MEGAJOULES
0.0
1.6
3.2
4.8
6.4
8.0
TIME / 10^6s

Fig. 9c.

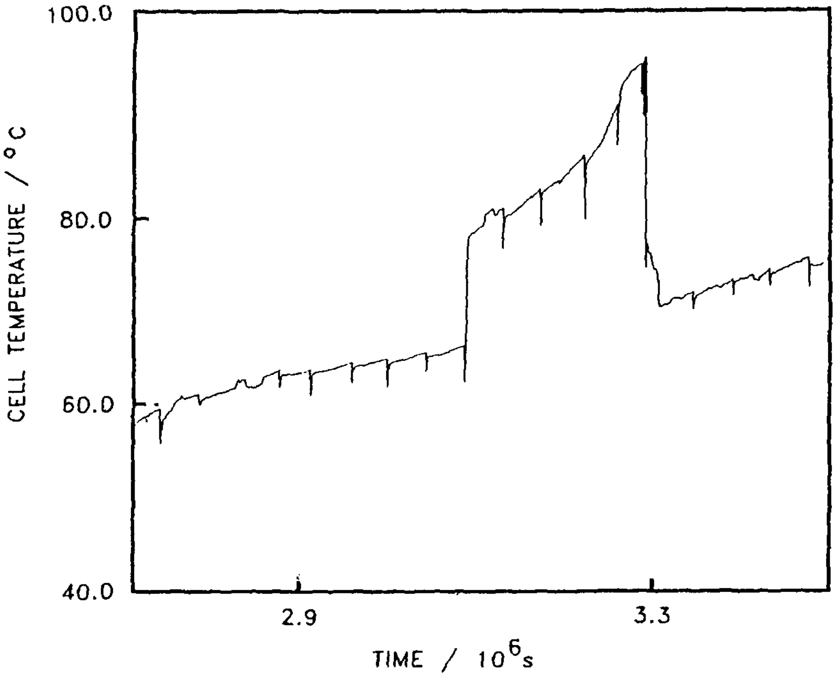


Fig. 10.

The discussions that follow refer to the papers presented at the workshop, not the paper submitted here for publication.

DISCUSSION (FLEISCHMANN)

Mansour: Why would you expect to find the deuterium at the octahedral sites in the palladium?

Fleischmann: That is where there is most room. You would also expect it to go to the grain boundaries and defects.

Mansour: Is light hydrogen known only to exist at large sites, and based on what data?

Fleischmann: There are some low-temperature neutron diffraction data on these systems, so the information is reasonably well known. The general opinion is that the octahedral sites are occupied by deuterons.

Appleby: In reference to the depth of the energy wells occupied by deuterons, do we have data on the activation for energy for deuterium diffusion in palladium?

Fleischmann: I do not know the value under these extreme loading conditions, at high PdD ratios.

Bockris: For hydrogen in iron, it is about 5 kcal/mole.

Appleby: That value is about 8 kT, which is not as low as your classical hindered translational model seems to suggest. The well depth suggests quantized energy levels, as do the separation factors.

Chubb: The diffusion coefficient value is a function of the deuterium concentration. At low concentration, it is two times greater for D in Pd than for H in Pd.

Fleischmann: The diffusion coefficient for the deuterium in the palladium lattice is higher than that for hydrogen, which is a strange phenomenon. It is also higher than that for surface diffusion. I would say that you cannot explain these phenomena unless you assume the bosonic character of the deuteron and leave the question to the quantum mechanical theoreticians.

Bockris: Based on normal considerations, I would expect light hydrogen to have the greater diffusion coefficient.

Fleischmann: I agree, but there is no doubt that D diffuses faster than H in the lattice and is faster in the surface at high concentrations by about a factor of two.

Chubb: In addition, the superconducting temperature range is 2 K higher for PdD than for PdH, which runs counter to all traditional views on isotope effects.

Huggins: We repeatedly discuss these systems as fast mixed conductors. However, for hydrogen in metals such as palladium, the diffusion coefficient is so high that one cannot use the normal lattice oscillator jump model for the diffusion process. In essence, almost every vibration becomes a successful jump. Thus, one must use some kind of a cooperative motion model with very low shallow potential wells.

Teller: When you have diffusion in a thin palladium layer, the effect of solubility may also make a difference. Protons may easily enter but may have difficulty leaving, whereas deuterons might easily go both in and out.

Fleischmann: It is important to carry out a reexamination of the diffusion of hydrogen, deuterium, and tritium, as a function of loading. The solubility of tritium also requires study.

Teller: This would be very important, and it is also of practical value. For example, experiments were conducted at Livermore some years ago on H/D and D/T separation, or deuterium and tritium.

Lewis: I have some data with me on the activation energy for diffusion of deuterium in β-phase PdD. The value is 5.7 kcal/mole. In addition, the equilibrium ratio of solubility of hydrogen to deuterium in palladium is 10, though the ratio varies somewhat with pressure. Hydrogen is therefore more soluble by about a factor of 10 at the same pressure.

Appleby: How do you reconcile the 5.7 kcal/mole value with classical potential wells? The energy levels should be quantized.

Fleischmann: It would depend on whether or not there is localized motion. The argument concerning the separation factor is based on the local behavior of the system.

Teller: Did you say that there was evidence for more than two deuterons on one side of an octahedral site and that condensation to a metallic phase might be favored?

Fleischmann: More than two may perhaps be accommodated. I don't want to go as far as saying that there is a free condensation to a metallic state, but I think it might be favored with deuterium.

Teller: This would be important, and it is relatively open to experimental investigation. At high densities the solubility of the deuteron should become greater than the solubility of the proton.

Fleischmann: Yes, there should be an inversion.

Teller: I am confused by your statement that the process is aneutronic and produces no tritium. In fusion, there are two parallel reactions: one producing neutrons, and the other producing tritium. If the process is aneutronic and produces no tritium, then you have nothing.

Chubb: Using the bosons in, bosons out rule, one could produce α-particles, which are bosons.

Lewis: Would you be satisfied with α-particle production, with no radiation?

Teller: Yes, but it is peculiar that there seems to be almost no radiation produced, which is a real contradiction. However, it is possible to obtain soft radiation in the ke V region, rather than in the Me V range.

Chubb: Alpha particles may have been detected at the Naval Research Laboratory in the higher energy range by George Chambers and coworkers. Their results were reported at the Santa Fe meeting and will appear in the conference proceedings. The results cannot be viewed as conclusive because of a later failure in their detector.

Teller: Low radiation and low neutron counts are very much outside of what is usually observed. However, α-particle production is not something that I would try to exclude.

Lewis: Have you had any problems with ignition of palladium? We have experimentally observed that palladium charged with hydrogen will melt on exposing it to oxygen.

Fleischmann: Our electrodes have never ignited.

Lewis: May I say one thing about your calorimeter calibration? I understood that you have a temperature-dependent quadratic term for radiation, plus a linear term for conduction. The heat transfer equation is therefore complex. However, you use only one temperature difference data point to determine the functional form of the equation. Is this enough to show that the $[T(^\circ K)]^4$ term dominates, or are independent experiments required?

Fleishmann: At low temperature differences, the expression linearizes.

Hoffman: Granted that your calibrations and measurements of the heat out are absolutely correct, is this always so for the heat in? A true RMS voltmeter is rarely used for galvanostatic measurements. If there is any surging due to arcing, a normal volmeter will not respond to it.

Fleischmann: The electrical system is under feedback control, so it will be extremely difficult for this system to show any surging.

Bockris: We have measured ac effects in our equipment, and we have seen about 4mV.

Lewis: The value would depend on the potentiostat, if it is used, and whether or not it is stable.

Fleischmann: Our system is stabilized against oscillation, which was one of our first precautions to obtain accurate results.

Jordan: When you said that you had at most 1 percent loss of gas by recombination, did you in fact collect the gases and measure this?

Fleischmann: Yes, we collected the gases. The effect of recombination was negligible.

Oriani: In what sense are deuterons, i.e., positive charges, present in the lattice? They must be tightly screened by electrons. How does one understand multiple occupancy of a lattice site where each species is creating a total volume expansion? Measurements of the volume of the entities in the lattice exist.

Fleischmann: There is a problem here. The concentration of deuterons or protons in the lattice is more than that in solid hydrogen. The concentration of electrons is comparable to that in silver. As one adds s-electrons, and if there is screening, one would expect the electric field gradient at the nucleus core to depend on the deuterium concentration in the lattice. A field gradient can only occur via the s-electron wave function, and we have nuclear magnetic resonance measurements. If you had a high density of deuterons and an excess chemical potential of 0.8 eV, you would expect to obtain D_2. Since that species is not formed, one probably does not have the electric field gradient. There is in fact tetrahedral distortion and an asymmetrical electric distribution.

Rafelski: Another possible explanation is that there is very asymmetric distribution of the electrons about the deuterons.

Oriani: Instead of D_2, why can you not form D^-?

Fleischmann: Some of our unpublished work shows that one can produce D^-.

DISCUSSION (PONS)

Bard: You reported originally that you used Newton's law of cooling to estimate heat flow as a function of temperature, which would give a linear dependence on temperature difference. Now you are stating that radiation, not conduction, is the primary heat loss mode, so that the Stefan-Boltzmann law with a $[T(°K)]^4$ temperature dependence term applies. Why have your assumptions changed from those in your original argument?

Pons: For small temperature differences, it does not make a significant difference whether you use a conductive or radiative heat transfer coefficient, since the higher terms in the latter linearize.

Bard: I am referring to the assumptions which you made in your presentation at the American Chemical Society meeting in April.

Pons: In April, there was a lack of understanding of the heat transfer coefficient using the linearized Stefan-Boltzmann law, as some questioners admitted. Since the calorimeter operated at low temperature differences, we used an expression of heat-conduction type to explain the simple heat transfer coefficient.

Lewis: Did you use the Stefan-Boltzmann expression to treat the original data?

Pons: We have always considered both radiative and conductive terms. Our calorimeters operated at low temperature differential, and the expression which we used then is what I indicated.

Lewis: Do you have experimental data on the calorimeter showing varying electrical power input into a resistor which demonstates the form of the heat transfer function?

Pons: Yes, those data are in our paper.

Jordan: You extrapolate your calorimetric response back approximately 45 h. Are you limited to doing this because the experiments last many days?

Pons: We extrapolate back to the time that solvent is added. This time is dependent upon how rapidly the D_2O is being consumed. At very low current densities, it may be several days before an addition is made to the electrolyte bath. At high current densities, additions are made perhaps twice per day.

Lewis: In one case, your cell temperature was 32.8°C. What was the bath temperature?

Pons: In that experiment it was 29.86°C.

Lewis: With only a 3°C temperature difference between the cell and the bath, does radiation still dominate heat transfer?

Pons: Yes.

Lewis: That seems to be unusual.

Huggins: How long is your calibration pulse?

Pons: The heaters are on for three hours for calibration.

Chu: Why does the voltage of the cell fall?

Pons: Because the temperature of the cell increases.

Bard: Did you use an oscilloscope to check for ac effects?

Pons: Yes, we observed 4 mV of oscillation.

Chu: How much excess energy did you see over the period of 8 million seconds?

Pons: About 16 MJ.

Chu: That represents more than 100 percent excess heat. What is the maximum current density which you have used?

Fleischmann: We have results up to about 5 A/cm^2.

Rafelski: When did the major excess heat event occur?

Pons: It occurred on August 1. However, the cell is still operating.

Oriani: In your excess heat results, do you subtract the 1.53 V, representing the heat of decomposition of heavy water, from the cell voltage?

Pons: The integral which I showed did have 1.53 V subtracted. In that particular cell, the gas recovery was better than 99 percent. We know how much D_2O was added. We know the cell current. The gas produced was equivalent to the heavy water added to within 1 percent. I should point out that if the excess heat is as high as that I have shown, it does not matter if 1.53 V is subtracted.

Bockris: Concerning excess heat per unit volume, at Texas A&M we consistently obtained 10-20 W/cm^3 on small electrodes. On larger electrodes results were still relatively consistent but were much lower, about 3-4 W/cm^3.

Pons: Our results on small electrodes, expressed in W/cm^3, were approximately the same as those at Texas A&M.

Bockris: Do you at present maintain that the effect is in the bulk palladium, so that W/ml units are indeed those which are appropriate?

Fleischmann: Our experimental goal was to obtain results on 1, 2, 4, 8, 12, 16, and 20 mm diameter rods to answer that question. We approached experiments on the larger rods with care, because a large electrode melted in our previous work. As it turned out, the time required for experiments on even 8 mm rods is enormous. They take three months to charge with deuterium, and we have yet to make one of these produce excess heat. We have no idea if a 2 cm diameter rod would be successful.

Menlove: During your experiments, did you monitor any fusion products apart from excess heat?

Pons: Yes. The maximum tritium level which we saw was eight times background. With simple equipment, we are looking for neutrons.

Fleischmann: We see 2.38 MeV gamma radiation when the cell is producing excess heat, as you can see on our spectrum, which includes 2.223 MeV.

Rafelski: Did you look for helium?

Pons: We are not ready to discuss our helium results, which are tantalizingly ambiguous. We have had "blank" difficulties.

Santucci: Did you sample the gases produced by electrolysis for helium?

Pons: It is not impossible to do that, but it is extremely difficult. Even if one first recombined the D_2 and O_2, it would still be difficult.

Gajewski: Do you attribute the high heat output which you have reported in your most recent cell to some special treatment?

Pons: No. I think that the heat burst outputs which we report are now measured accurately because we now have an excellent mathematical model to describe the calorimeter.

Lewis: What percentage of your small electrodes have produced excess heat?

Pons: The electrodes which we showed as blanks did not produce excess heat. We have examined a total of about 30 electrodes.

Thompson: It might be interesting to state that we have seen a consistent feature of all of the rods which proved to be positive. We have noticed a difference in the 8 mm rod returned from the University of Utah. The microstructure of the 1, 2, and 4 mm rods appears to be identical, although it requires more painstaking metallography to complete the analyses. There is a significant difference in the 8 mm rod, which was operated for approximately the same period of time as the others.

Huggins: What is the difference?

Thompson: The microstructure of the small rods is consistent with the drawing process used for forming, whereas that of the 8 mm rod has a much smaller granular structure. Whether this was caused by the long period of charging with deuterium or whether it was there initially has yet to be determined.

Santucci: What type of metallurgical tests have you carried out on the 1, 2, and 4 mm diameter cathodes?

Thompson: We have looked at transverse and longitudinal sections of the palladium rods. The structure is absolutely consistent with what a metallurgist would expect from a rod which has been cast, forged, and then drawn, which is our standard production process. This has been used for the rods that we have supplied either commercially or to various research laboratories, including the University of Utah.

Santucci: So there are no changes that can be attributed to the excess heat effect?

Thompson: We have noticed significant recrystallization in two of the rods which produced excess heat. On rods which had been operated at 512 mA/cm^2 for long periods, XRD analysis showed that the amount of deuterium remaining was significantly lower than that in a rod charged at 64 mA/cm^2. Perhaps, the two results together may be interpreted as meaning that more excess heat was generated in the first rod than in the second.

Rafelski: Did both of the rods produce excess heat?

Thompson: Yes.

Santucci: When you say substantial recrystallization, do you mean around the bulk material or in the surface skin?

Thompson: The recrystallization was at one end of the rod. I hesitate to give further details because of the limited number of samples which we have examined. We have only examined five specimens altogether.

Bockris: Did you examine the rods for cracking and fissure formation?

Thompson: We found cracks and scratches to be surface features of virgin rods. The intensity of these features increases with the use of increasing current densities.

Bockris: Can you tell us anything about these tantalizing helium results?

Thompson: We provided samples of these for analysis externally. We have not yet received complete analytical results.

Myles: Can you describe the origin of the palladium?

Thompson: Our main supplier is South African.

Myles: What is the origin of these specimens, since this is a critical point?

Thompson: I have not been asked that question before. As far as I know, the palladium would have been of South African origin.

Kim: (to Dr. Pons) What ratio of tritium production to neutron production have you observed?

Pons: The levels which we have measured have been too small to make any reliable estimate.

Fleischmann: Without question, there was much more tritium production compared with that for neutrons. The most reliable results so far on this ratio are from Bhabha Atomic Research Center (BARC) in India.