

# EXPERIMENTAL CONSIDERATIONS IN ELECTROCHEMICAL ISOPERIBOLIC CALORIMETRY

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## ABSTRACT

A novel concentric cylinder isoperibolic calorimeter was designed and fully characterized. Several different methods of introducing calibration power to the calorimeter were studied and the calibration constant was found to be independent of the method. Calibration constants could be determined with a precision to  $\pm 0.5\%$ . Furthermore, they were independent of the input power level up to 22 W and with a cell temperature up to 60 °C over appreciable periods of time. This new design possesses many advantages that makes it suitable for careful studies of the thermal behavior of electrochemical systems, such as the electrochemical insertion of deuterium into Pd cathodes.

## INTRODUCTION

Calorimetric techniques have widely been used to study thermochemical properties of both static and reacting systems with great success. A great deal of attention has been drawn to this experimental method recently as a result of the announcement by Fleischmann and Pons last year [1] that they had observed the generation of large amounts of excess heat when deuterium is electrochemically inserted into palladium. This paper describes the design and performance characteristics of a new type of isoperibolic calorimeter that has been employed for heat flux measurements during the electrolysis of both light and heavy water upon palladium cathodes.

The word "isoperibol" denotes uniform surroundings. So, isoperibolic calorimetry refers to methods in which thermal energy is transferred from a heat source to a surrounding heat sink that is maintained at a constant temperature. It is generally

operated in a steady state power balance mode. When applied to electrolysis systems, heat is typically generated within the electrochemical cell and transferred through a intermediate thermally-conducting layer to a surrounding water bath held at constant temperature. Under steady state conditions, a temperature distribution is established in which the temperature difference across the thermally -conducting layer transports heat at a rate that just balances the power generated within the electrochemical cell. Thus, in principle, measurement of the temperature difference between the cell and the surrounding bath provides information about the thermal power generated in the electrochemical cell,  $P_{\text{therm}}$ . This can be simply expressed as

$$P_{\text{therm}} = K (T_1 - T_2) \quad (1)$$

where  $K$  is the calorimeter calibration constant, and  $T_1$  and  $T_2$  are the temperatures of the cell and bath.

As will be shown below, if the electrical power applied to the cell causes a chemical or electrochemical reaction to occur that involves a change in the enthalpy of the system, the thermal power generated  $P_{\text{therm}}$  is not equal to the applied electrical power  $P_{\text{appl}}$ . This is described as a thermodynamically "open system", and is the case if the gaseous products of the electrolysis reaction are allowed to escape. As a result, the temperature difference between the cell and the surrounding bath is less than it would be if the applied electrical power produced only Joule heating.

On the other hand, if a thermodynamically "closed cell" design employing an in-cell recombination catalyst is used, so that no enthalpy is transported out of the system,  $P_{\text{therm}}$  and  $P_{\text{appl}}$  will be equal if

there is no other heat generation or absorption process present. This is thus a conceptually simpler situation, and any measured difference between the input and output powers must have some other origin. One possibility is that it might be due to some additional power generation process taking place inside the electrochemical cell, as proposed by Fleischmann and Pons [1].

## CALORIMETER DESIGN

A new type of isoperibolic calorimeter has been designed in which various issues such as the influence of the physical locations at which heat is produced and at which the temperatures are measured during both calibration and operation, and the magnitude of the stirring of the electrolyte fluid are not relevant.

The new design consists of two concentric heavy aluminum cylinders that are separated by a well-defined thermally conducting layer. The electrochemical cell fits snugly inside the axial hole of the inner cylinder. Under steady state conditions, essentially all the heat generated within the electrochemical cell passes to the external environment radially through the surrounding cylinders.

Instead of relying upon measurement of the temperature within the electrochemical cell itself, as well as of the assumed homogeneous environment, this design involves the measurement of the temperatures of the two aluminum cylinders. Because of their dimensions and excellent thermal conductivity, the aluminum cylinders provide temperature uniformity. Thus possible sources of error related to issues such as the amount of stirring and the locations of the heat sources and temperature measurement within the electrochemical cell are avoided.

The design of this new isoperibolic calorimeter is shown schematically in Figure 1. The inner ( $T_1$ ) aluminum cylinder has an outer diameter of 2 inches and an inner diameter of 1.17 inches. It is 4 inches long, and weighs about 365 g. The outer ( $T_2$ ) aluminum cylinder is 7 inches long and weighs 958 g. Its inner diameter is 2.25 inches, and its outer diameter, 3.0 inches. Thus the gap across which the heat conduction takes place, and the temperature difference is measured, is 0.125 inches. The container for the electrochemical cell that fits snugly inside the ( $T_1$ ) cylinder is a quartz tube 1.14 inches (29 mm) in outside diameter and 4 inches long.

The inner ( $T_1$ ) cylinder housing the electrochemical cell is mounted on Teflon supports and placed concentrically inside the outer ( $T_2$ ) cylinder in such a

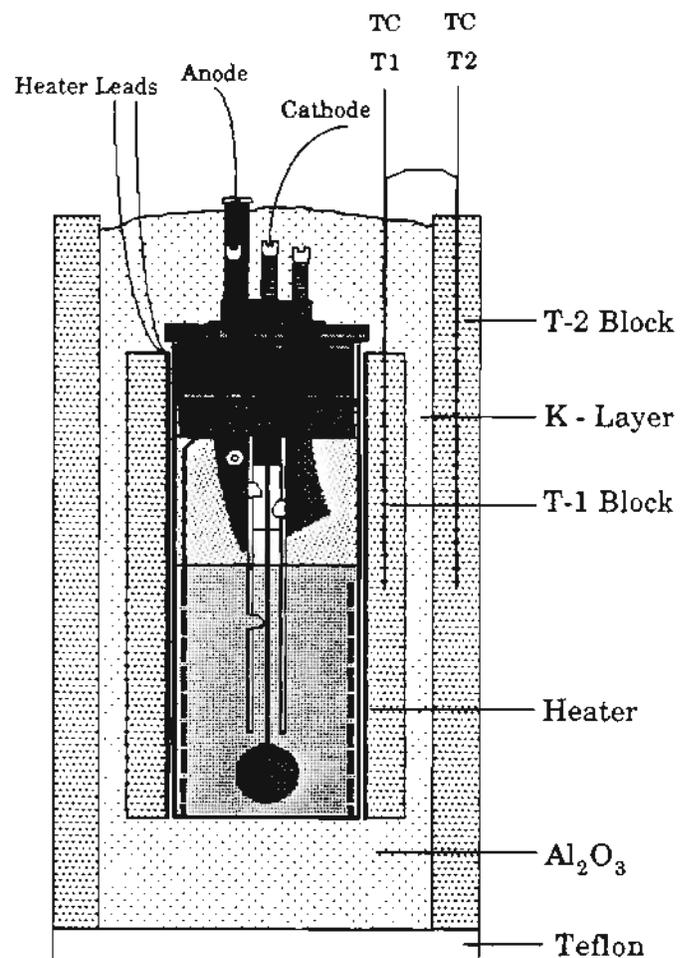


Figure 1. Schematic design of the concentric cylinder isoperibolic calorimeter with the external thin sheet Joule heater wrapped around the electrochemical cell and inserted inside the inner aluminum cylinder.

way that 1.5 inches of vertical space is left above and below the inner cylinder. This vertical space above and below as well as the 0.125 inch wide radial gap between the two cylinders is packed with  $Al_2O_3$  powder. This thick layer of  $Al_2O_3$  powder insulation above and below the cell and inner cylinder forces the heat to be transferred in the radial direction across the gap between the two cylinders. The effective thermal conductivity of this  $Al_2O_3$  powder, which has a particle size range of 50-200 mm, was experimentally determined to be about  $1.6 \times 10^{-3}$  W/cm. $^{\circ}C$ .

Three small thermocouple holes 1/16 inches in diameter were drilled vertically down to half-height of each aluminum cylinder. The holes are located at midpoints of the wall thickness of the cylinders and

are spaced 120° circumferentially from each other. Copper-constantan (Type T) thermocouples were firmly fixed into these holes so as to make good physical contact with the aluminum. A few drops of silicone oil were put at the bottom of these holes to enhance the thermal contact between the thermocouples and the aluminum cylinders. The thermocouples are used in a differential mode such that each calorimeter contains four pairs of thermocouples. In each case, the outer members are copper, so as to avoid any thermoelectric effects when they are joined to the measuring circuitry. Two pairs are connected between the inner ( $T_1$ ) and outer ( $T_2$ ) aluminum cylinders to sense the temperature difference between the cylinders. The other two pairs of thermocouples are connected between each aluminum cylinder and the surrounding constant temperature water bath. Thus all possible adverse thermoelectric contributions from dissimilar contacts are eliminated. The linear response of these T-type thermocouples is 39 mV/°C. A 6 1/2 digit Keithley Model 193A microvoltmeter is used for reading the thermocouple output and it thus provides a resolution of about 0.025 °C.

Eight such calorimeters have been built and tested. Their 1/e time constants were determined from their transient response to step changes in the level of the input power, and were found to range between 13 and 15 minutes.

## ELECTROCHEMICAL CELL DESIGN

The electrochemical cells used in this work are thermodynamically "closed" cells, i.e., they contain an internal recombination catalyst made of finely divided Pt supported on Teflon with a nickel backing to recombine the  $D_2$  and  $O_2$  formed by the electrolysis and return it by gravity back into the electrolyte. In contrast, the gaseous products of electrolysis are vented off to the outside in "open" cells.

The cells were connected externally to silicone oil bubblers by plastic tubing. This served two purposes. One is to prevent atmospheric moisture to diffuse back into the electrolyte of the electrochemical cells, which contain about 20 ml of 0.1 M LiOD in  $D_2O$ . This is an important consideration since  $D_2O$  attracts light water strongly, and hydrogen is selectively absorbed into the Pd cathode. The other reason for the bubbler is to allow the escape of gas in the amount of uncombined oxygen. Observation of the time behavior of the bubble evolution provided information about this process, and showed that it ceased as the Pd cathode became saturated with deuterium.

The Pd cathodes were prepared by repeated arc melting in a gettered argon atmosphere, followed by mechanical deformation to produce a "fat dime" shape. Earlier, thin Pt and Au wires were used to make electrical connections to the Pd cathodes. However, due to surface contamination problems, the cathode current collector was changed to fine Pd wire, which was shielded by a thin Teflon tube to prevent appreciable electrolysis taking place on it, rather than on the Pd cathode.

Three different cell designs have been studied. In the first design, a static immersion heater shielded in J-shaped quartz tubing was used to provide the Joule heating for calibration. The cell was sealed with a rubber stopper, which housed the feed-throughs for cathode and anode lead connections, the immersion Joule heater, and the gas vent to the silicone bubbler. The anode was about 200 cm of 0.010 inch thick Pt wire spirally wound inside the cell. The anode to cathode surface area ratios were between 10 and 15 to assure that most of the applied voltage drop was at the Pd cathode.

Although this general design provided reproducible calibration and stable electrochemical performance, the problems associated with the cramped space inside the cell as well as in the rubber stopper and the occasional and unpredictable breakage of the quartz shielding around the Joule heater led to a modified design.

Energy dispersive spectroscopy studies of the surface of the Pd cathodes indicated the presence of substantial amounts of Pt coverage, which can block deuterium insertion. Therefore, the fine wire Pt anodes were replaced by large surface area thin Pd ribbon anodes, produced by rolling 1/8 inch O.D. Pd wire. This modification has the advantage of continuously depositing fresh Pd upon the cathode surface, which could cover up any potentially blocking metallic or other impurities that might be deposited during the electrolysis process.

The second design used a modified three-electrode configuration, in which heat generated by electrolysis upon an auxiliary Pt wire cathode centered within the cell was utilized for calibration purposes. Passing current between this Pt cathode (instead of the Pd cathode) and the Pd anode caused only the generation of Joule heat, so that measurement of the electrical input to this configuration provided a simple calibration method, with gas generation, bubble-driven stirring, and recombination similar to that which takes place during electrolysis with the Pd cathode. Of course, one had to be sure to open the Pt cathode circuit during operation of the Pd cathode to insure that there was no electrical cross talk between

the two cathodes. Again, rubber stoppers were used to support the electrical feed-throughs and the gas vent to the bubbler.

The third design used a simple Pd cathode and Pd ribbon anode arrangement inside the cell. Joule heater power for calibration was provided by a thin film sheet heater which was snugly fitted between the outside of the quartz cell and the inside of the inner aluminum cylinder of the calorimeter. Rubber stoppers were abandoned because of concern about their possible contamination of the electrolyte, and were replaced by cell caps machined out of Delrin.

## EXPERIMENTAL PROCEDURES

### Calorimeter Calibration Principles

The basic equation for an isoperibolic calorimeter was given earlier as equation (1), which relates the thermal power output to the measured temperature change through the calibration constant, K. In the current design, the value of K is determined by the construction of the concentric cylinder calorimeter, and is independent of the particular experiment being performed within it.

The most common way of supplying the power for calibration is by the use of an internal Joule heater. Several levels of electrical power are applied, and the corresponding increases in the steady state temperature evaluated. A plot of  $(T_1 - T_2)$  versus applied electrical power gives a linear relation, whose slope is the reciprocal of the calibration constant K.

However, it is often desirable to perform a calibration of the calorimeter while electrolysis is also taking place. In that case, the total applied thermal power introduced is the sum of that which is provided by the Joule heater and that contributed as a result of the electrolytic process. In addition, we must consider the possibility that there may also be another phenomenon present that introduces additional thermal power,  $P_{int}$ .

In the absence of any other energy generating or consuming effects, so that  $P_{int}$  is zero, electrolysis conducted in a "closed" cell in which the gaseous products of the electrolysis are internally recombined, produces exactly the same results as a simple Joule heater [2-4].

This is not true in the case of an "open" cell, however, as enthalpy is carried out of the system by the escape of evolved gases. Therefore the contribution to  $(T_1 - T_2)$  due to the electrical power applied to the electrolysis process will be lower than if the same amount of power were applied to a simple

Joule heater, and the apparent value of K would be greater than the proper one.

There is an additional effect that must be considered in order to obtain a proper calibration of a calorimeter by adding Joule heat in the presence of electrolysis. This is because changes in applied Joule heater power cause changes in the temperature of the electrolyte. This causes changes in electrolyte resistance, and can thus influence the amount of thermal power introduced in connection with the electrolysis reaction.

As an example, if additional heater power  $\Delta P_{hr}$  is applied, the electrolyte temperature will increase. Because of this increased temperature, the overall cell resistance decreases.

If the electrolysis is being conducted under constant voltage conditions, the electrolysis current will increase. This increases the electrolysis thermal power input by an amount  $\Delta P_{el}$ . On the other hand, if the electrolysis is conducted under constant current conditions, the voltage and the thermal power introduced by the applied electrolysis power will both decrease.

Thus we see that the total change in thermal power introduced into the calorimeter is the sum of two factors, that simply due to the added calibration heater power  $\Delta P_{hr}$ , and that due to a change in the electrolysis power  $\Delta P_{el}$  due to the concomitant decreased electrolyte resistance.

Therefore, we can not merely compare the observed value of  $(T_1 - T_2)$  to the sum of the electrical power applied to the heater and that applied to the electrolysis reaction. We must separate these two effects. The total power,  $P_{tot}$ , put into the cell during calibration while electrolysis is also taking place is

$$P_{tot} = P_{hr} + P_{el} + P_{int} \quad (2)$$

Additional Joule heater power increases the temperature difference  $(T_1 - T_2)$  by  $\Delta T_{hr}$  such that the total temperature rise,  $\Delta T_{tot}$ , is given by

$$\Delta T_{tot} = \Delta T_{hr} + \Delta T_{el} + \Delta T_{int} \quad (3)$$

where  $\Delta T_{el}$  is the change in  $(T_1 - T_2)$  due to the change in the electrolysis power, and  $\Delta T_{int}$  is the change in  $(T_1 - T_2)$  due to any related change in the additional internal heat generation process, if one is present.

We can also write

$$\Delta T_{\text{tot}} = \Delta P_{\text{hr}}/K + \Delta P_{\text{el}}/K_{\text{el}} + \Delta P_{\text{int}}/K_{\text{int}} \quad (4)$$

if the values of  $K$ ,  $K_{\text{el}}$  and  $K_{\text{int}}$  are not the same. In that case, we note that (4) is not the same as

$$\Delta T_{\text{tot}} = (\Delta P_{\text{hr}} + \Delta P_{\text{el}} + \Delta P_{\text{int}}) / K \quad (5)$$

which would be the case if all the  $K$  values were the same.

The apparent value of  $K$  that would result from this experiment is given by

$$K_{\text{apparent}} = (\Delta P_{\text{hr}} + \Delta P_{\text{el}} + \Delta P_{\text{int}}) / (\Delta T_{\text{hr}} + \Delta T_{\text{el}} + \Delta T_{\text{int}}) \quad (6)$$

which can be quite different from the real value characteristic of the calorimeter,  $K$ .

This problem can be solved by assuming that  $\Delta P_{\text{el}}$  and  $\Delta P_{\text{int}}$  are coupled, and can be represented by a single value of  $K_{\text{el}}$ , which can be found from the values of  $(T_1 - T_2)$  and  $P_{\text{el}}$  in the absence of any heater power. If the magnitude of  $K_{\text{el}}$  varies with electrolysis power level, it can be determined over any desired power range by performing an additional experiment, in which the value of this composite  $K_{\text{el}}$  is determined by observing the change in temperature difference  $(\Delta T_{\text{el}} + \Delta T_{\text{int}})$  that results from a change in the electrical power input  $\Delta P_{\text{el}}$  applied to the electrolysis process. For that case,

$$K_{\text{el}} = \Delta P_{\text{el}} / (\Delta T_{\text{el}} + \Delta T_{\text{int}}) \quad (7)$$

Thus if we have the value of  $K_{\text{el}}$  we can find the proper value of  $K$  for the calorimeter from

$$K = \Delta P_{\text{hr}} / (\Delta T_{\text{tot}} - (\Delta T_{\text{el}} + \Delta T_{\text{int}})) \\ = \Delta P_{\text{hr}} / (\Delta T_{\text{tot}} - (\Delta P_{\text{el}} / K_{\text{el}})) \quad (8)$$

An alternative strategy is to operate the cell in a different mode, maintaining the electrolysis power constant, with the computer, rather than keeping the electrolysis voltage constant. If we did this, the electrolysis power would not go up when the heater power is introduced, and the observed temperature rise would be due to the effect of the heater power alone. This would allow direct evaluation of  $K$  without the need for a separate experiment to evaluate  $K_{\text{el}}$  and to separate out the two factors.

However, if the electrolyte temperature increases, and thus its resistance decreases, as the result of the addition of heater power, the relationship between electrolysis voltage and current will change, even under constant electrolysis power.

## Calibration Procedure

Experiments were performed to determine the values of  $K$  for the calorimeters using three different methods of introducing power, an immersion Joule heater within the electrochemical cell, internal electrolysis, and a Joule heater placed between the external wall of the electrochemical cell and the inside surface of the inner cylinder of the calorimeter. Each of these methods can be readily incorporated into the electrochemical cell design, as discussed earlier. The calibration procedure simply involved the introduction of several levels of Joule heating power, in both increasing and decreasing steps, and the measurement of the temperature difference between the two aluminum cylinders in each case. Calibrations were carried out both with and without concurrent "closed cell" electrolysis, and with the electrolysis conducted in either the constant power mode or the constant voltage mode. In the latter case, the corrections discussed above were applied.

## Measurement and Data Acquisition System

The power for both the electrolysis and the Joule heater were supplied by Lambda LLS series power supplies. In the case of constant electrolysis power, the power supplies for the electrolysis process were computer controlled. A Macintosh IIx computer was used for this purpose as well as for calorimeter data acquisition, using a Keithley 193A microvoltmeter and a Keithley 706 scanner. For each calorimeter, a total of ten experimental parameters were monitored. They included four differential and two absolute thermocouple values, as well as two voltage and two current (read as voltage across precision resistors) values. They were measured sequentially, and each point was averaged over ten readings and stored every 5 to 15 seconds. The hardware allowed five calorimeters to be monitored and controlled simultaneously. Both the cell operation and the data acquisition were controlled using the LabView software from National Instruments Co.

## CALIBRATION RESULTS

As mentioned earlier, the temperature distribution within the calorimeter is measured by the use of six copper-constantan (Type T) thermocouples located at different positions in the calorimeter. They were configured in a differential mode such that only the copper ends of each pair were connected to the microvoltmeter, eliminating spurious thermoelectric effects. Figure 2 shows the exceptional agreement between three temperature difference measurements, made at the six points in the calorimeter by the four

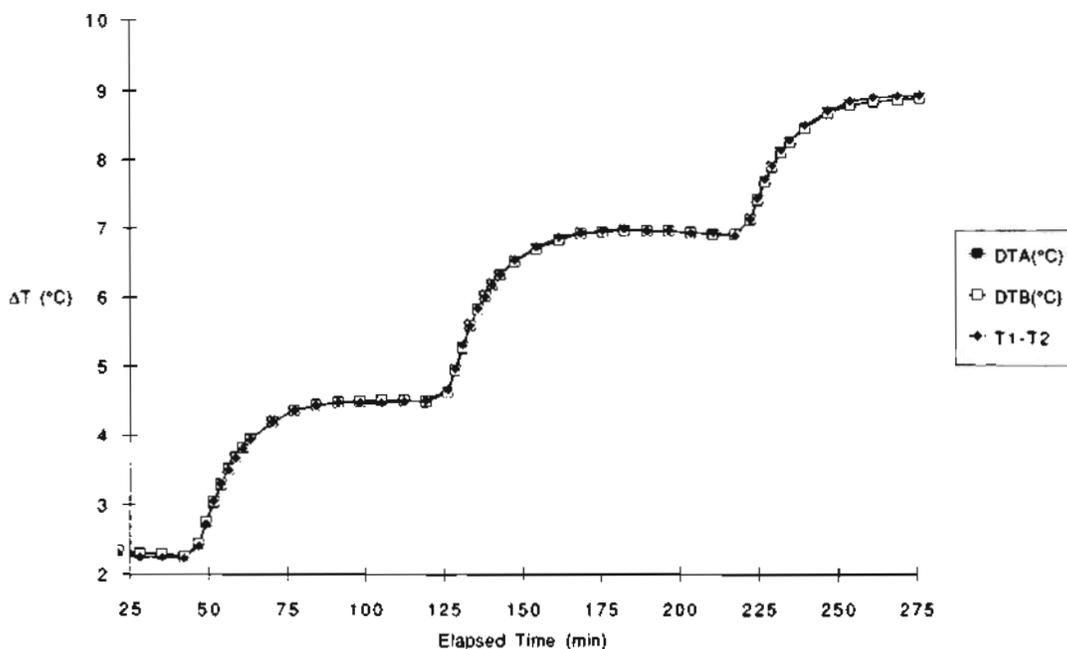


Figure 2. The variation of temperature with time during a calibration experiment at three levels of power input using an immersion Joule heater. All three differential temperatures measured at different locations lie exactly on top of each other indicating a uniform temperature distribution within the inner aluminum cylinder in the calorimeter.

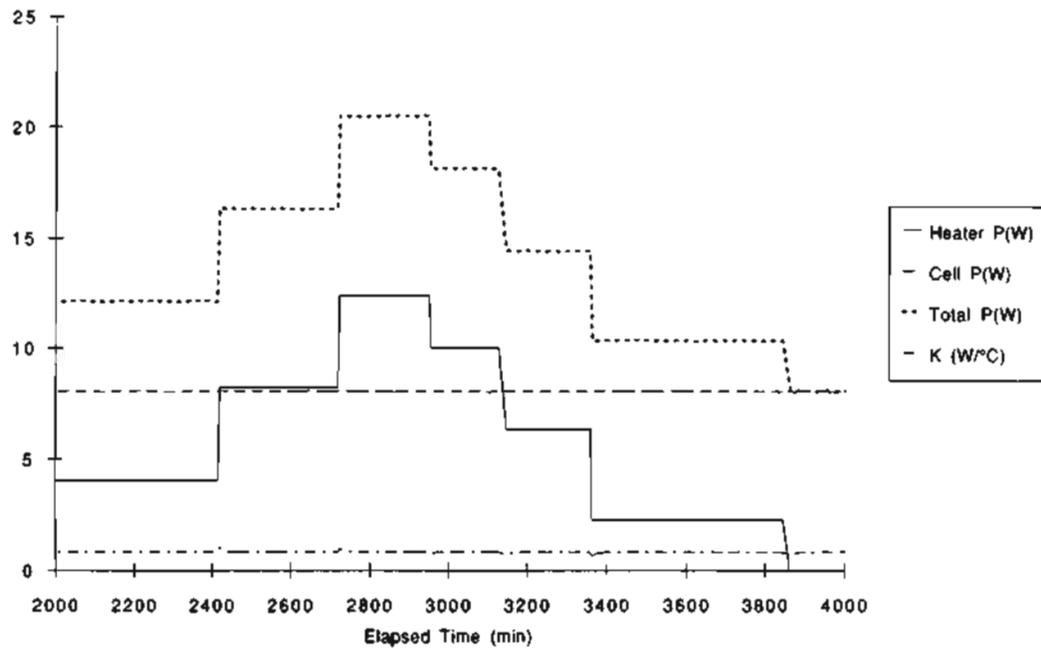
pairs of differential thermocouples, and clearly demonstrates the uniformity of the temperature distribution within the calorimeter. This is an important advantage. It eliminates any ambiguity about the locations of the sources of heat and the temperature probes within the electrochemical cell. Hence the extent of stirring to distribute the heat within the electrochemical cell becomes irrelevant.

These data also illustrate the typical time - dependent variation of the temperature during a calibration carried out by the use of an immersion Joule heater.

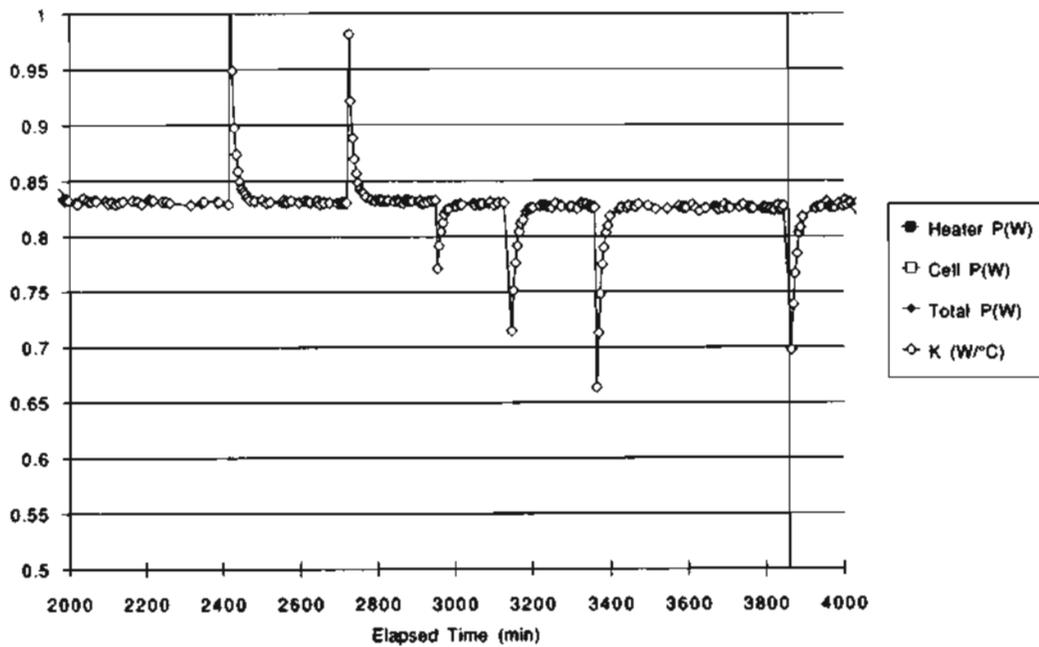
A typical time variation of the two electrical power inputs during a calibration experiment is shown in Figure 3(a). The Joule heat for calibration was supplied by a thin sheet heater external to the electrochemical cell, and the electrolysis was operated in the constant power mode in this case. Note that all are very flat and steady with time. High total power levels, sometimes in excess of 20 watts, as was the case here, have been commonly used in both our calibration and electrochemical insertion experiments.

The time variation of the calibration constant extracted from these data using equation (8) is shown in Figure 3(b). The spikes on the graph are due to the transient behavior of the calorimeter when the input power level is varied abruptly. The steady state behavior, however, clearly shows that the calibration constant values are very consistent, lying in a band less than 0.5 % wide, and independent of the input power level as well as time.

The effect of different modes of Joule heating during calibration experiments was also studied. It was found that the value of the calibration constant was independent of the manner in which power was supplied to the calorimeter. This is illustrated in Figure 4, which compares the results of experiments using the external thin sheet Joule heater with those using the electrolytic heater, both with and without simultaneous electrolysis taking place. Over a wide range of power levels the calibration constant was independent of the type of calibration heat source, and in this case was equal to 0.83 W/°C with a precision to  $\pm 0.5\%$ .



(a)



(b)

Figure 3. (a) The variation of Joule heater, electrolysis and total input power as a function of time during a calibration experiment using an external thin sheet Joule heater. The electrolysis was operated in the constant power mode. (b) The corresponding values of the calibration constant,  $K$ , as a function of time and the input power level. It is clear that  $K$  is practically independent of the input power level as well as time.

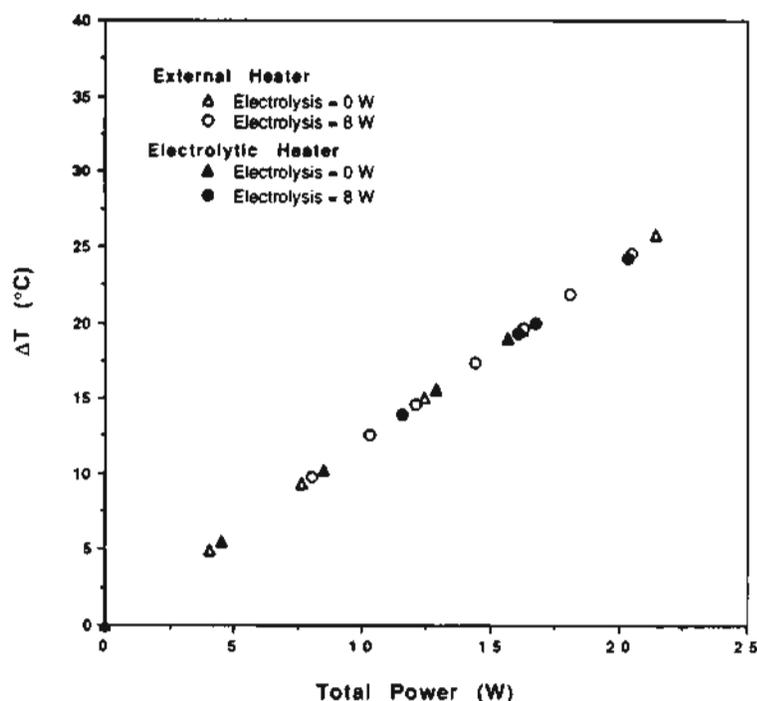


Figure 4. Calibration plot to compare two different ways of introducing calibration heat using external thin sheet and electrolytic Joule heaters both with and without electrolysis taking place.

The variation of the calibration constant with the cell temperature is also of interest. The data shown in Figure 5 indicate that  $K$  is practically constant over a wide range of temperature.

## DISCUSSION AND CONCLUSIONS

It has been shown that the novel concentric cylinder isoperibolic calorimeter design has consistent and attractive features, providing reliable information with a high degree of precision. The general design feature whereby heat is uniformly distributed throughout heavy aluminum cylinders, where the temperature measurements are made, eliminates the uncertainties associated with the exact nature and location of the heat source and the temperature probe. It also renders the issue of the adequacy of stirring irrelevant, and thus makes these calorimeters attractive for the study of the thermal characteristics of the electrochemical insertion of deuterium into Pd, as well as other electrochemical studies.

The major construction materials are aluminum and alumina, both of which allow operation at quite high temperatures, perhaps up to 600 °C. Materials used for the construction of the electrochemical cell will be

the major factor limiting the maximum temperature of operation.

Calibration has been conducted using three different modes of introducing calibration heat. The calibration constant was found to be independent of whether the power was supplied by an immersed Joule heater, internal electrolysis, or an external thin film Joule heater. This provides flexibility in experiments using this design.

Experiments on the time dependence of the response to step changes in the input power level have demonstrated  $1/e$  times of about 15 minutes. This enables one to observe relatively rapid changes in the thermal behavior of electrochemical systems.

The calibration constants have been found to be independent of both time, input power level, and cell temperature over quite a wide ranges, with uncertainties less than  $\pm 0.5\%$ .

This high level of precision makes it possible to accurately study questions such as the thermal behavior of Pd during the electrochemical insertion of deuterium.

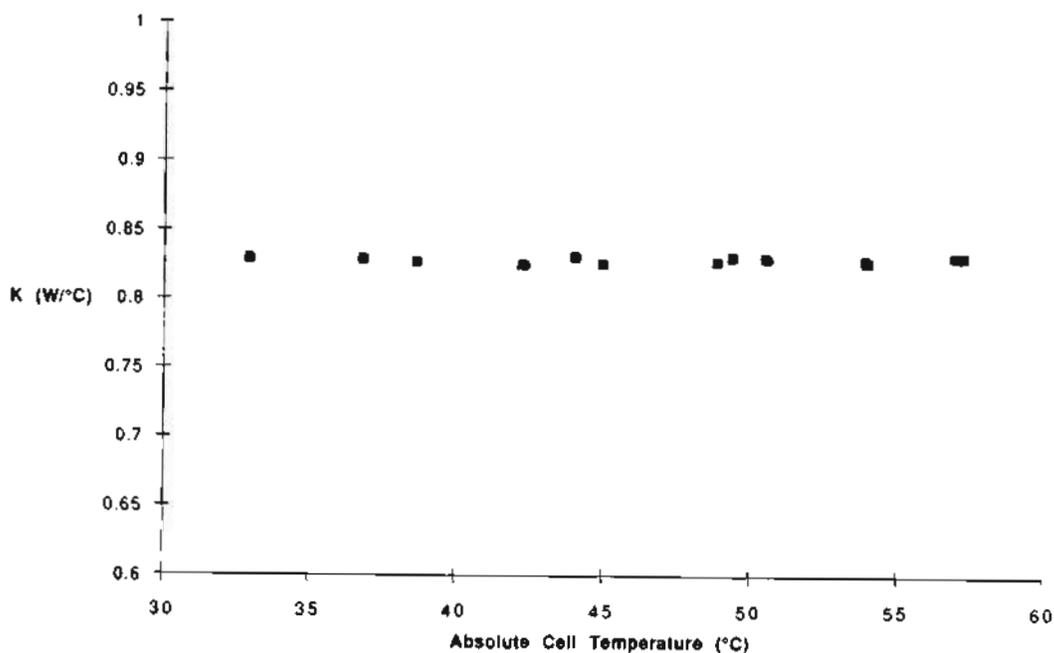


Figure 5. Temperature dependence of the calibration constant over a wide range of cell temperatures.

## ACKNOWLEDGEMENTS

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