

Electrochemical Isoperibolic Calorimetry For D₂O Electrolysis

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Abstract

Equations developed for isoperibolic electrochemical calorimetry were tested for the electrolysis of D₂O in an open calorimetric cell. The derivatives of these equations gave correct values within the experimental error range for the important rate of change of the cell temperature with time (dT/dt). In addition, these calorimetric equations were also tested directly in determining the enthalpy change (ΔH) for the D₂O electrolysis reaction. The mean experimental value at 298.15 K was $\Delta H = 294.4 \pm 0.3$ kJ/mole. This compares favorably (within 0.10%) with the literature value of $\Delta H = 294.600$ kJ/mole. The accuracy of these ΔH measurements could be even further improved by more accurate cell voltage and cell temperature measurement.

Introduction

The history of electrochemical calorimetry illustrates that this research has generally been a neglected scientific topic despite the many possible calorimetric applications in electrochemical research [1-5]. An excellent test for open isoperibolic calorimetric cells is the determination of the enthalpy change for the electrolysis of heavy water (D₂O). This research is complicated because even the simple electrolysis of D₂O at constant current (I) in open isoperibolic calorimetric cells gradually produces changes in the cell voltage (E), the cell temperature (T), cell constant (k), cell heat capacity (C_pM), electrolyte volume (V), and the cell power (P). Therefore, there is generally no steady state time period where dT/dt = 0 exactly.

Many of the calorimetric power terms in this study were first developed by Fleischmann and Pons for their measurements in the Palladium-D₂O + LiOD system using a Dewar calorimeter where heat transfer is mainly by radiation [6-8]. The author has reported related studies using calorimeters where the heat transfer is by conduction [9-12].

There are often significant calorimetric errors if the important term, $P_{\text{calor}} = C_p M dT/dt$, is ignored where C_p is the heat capacity of D₂O (84.35 J/mol K) and M is the equivalent moles of D₂O required to give the correct total heat capacity for the cell including the glass and metal components that undergo the same cell temperature changes as the D₂O. If the cell temperature changes by ± 0.1 K over 10 minutes for a typical cell heat capacity of C_pM = 450 J/K, then the calorimetric error, if dT/dt is neglected, is given by

$$\Delta P_{\text{calor}} = (450 \text{ J/K})(\pm 0.1 \text{ K})/(10)(60)\text{s} = \pm 0.075 \text{ W}$$

This ± 75 mW is a substantial error source for the electrochemical calorimetry. Even if the cell temperature change with time is only ± 0.01 K over 10 minutes, this would still be an important

error source of ± 7.5 mW. Accurate temperature measurements are necessary at various times for accurate electrochemical calorimetry.

Experimentally, it is found that dT/dt may be positive or negative for open isoperibolic calorimeters depending on the experimental conditions. The goal here is to derive equations for the calculation of dT/dt to gain a better understanding of the variables that determine this dT/dt value. These derived equations will also be a test for the basic calorimetric equations used to model the calorimeter. Several tests of these equations with experiments data will be presented.

The major test of this isoperibolic electrochemical calorimetry and the modeling equations is the experimental determination of the enthalpy change (ΔH) for D_2O electrolysis using these calorimetric equations.

Experimental

The calorimeter used in these experiments was constructed from commercial copper tubing and copper end caps [13]. The outer copper cylinder had a 5.1 cm (2.0 inch) diameter and a 28 cm height. The inner copper cylinder (3.2 x 20 cm) was completely separated from the outer cylinder by the insulating material. The glass electrochemical cell (2.5 x 20 cm) was a large Kimax test tube. This cell was filled 2/3 full, with 50.0 mL of the 0.1 M LiOD + D_2O electrolyte and securely centered within the inner copper cylinder. This calorimetric system can be described as isoperibolic, non-adiabatic and non-isothermal.

The D_2O used was Cambridge Isotopes, 99.9% D. Three thermistors were used for measurements of the cell temperature. One of these thermistors (T_1) was positioned in the cell electrolyte while the other two (T_2 , T_5) were securely fastened on opposite sides of the outer cell wall. The cell constants were $k_1 = 0.1205$ W/K, $k_2 = 0.1350$ W/K and $k_5 = 0.1450$ W/K. Thermal contact between the glass cell and the inner copper tube was provided by Mobile-1 (5 W-30) synthetic motor oil (35 mL). The total cell heat capacity was 450 J/K. This isoperibolic calorimeter was placed in a constant temperature water bath. Each calorimetric measurement recorded the cell current (I), the cell voltage (E), the cell temperature (T), and the bath temperature (T_b). The cell current was constant at $I = 0.1500$ A in most of these experiments. The temperatures were measured to within ± 0.005 K by the use of calibrated thermistors. These experiments used a platinum wire coil as the anode and a centered palladium or palladium-boron cathode [9-13]

Calorimetric Power Terms

Accurate open isoperibolic electrochemical calorimetry can involve up to eight different power terms. Power can be added to the cell by the electrochemistry (P_{EI}), by an internal heater (P_H), or possibly by some additional unknown power source (P_X) such as recombination. Power can be carried out of the cell by heat conduction (P_C), by heat radiation (P_R), by heated gases (D_2 , O_2 , D_2O) that exit the cell (P_g) and by the expansion work done by this gas production (P_W). The sum of these different power terms will generally produce a power change within the calorimetric system (P_{calor}). The connection between these power terms is expressed by

$$P_{calor} = P_{EI} + P_H + P_X + P_C + P_R + P_g + P_W \quad (1)$$

where power added to the cell is positive and power carried out of the cell is negative. No internal heater was used in these experiments ($P_H = 0$) and there was very little heat lost by radiation ($P_R \approx 0$) due to the cell insulation surrounding the cell including at the cell bottom and the cell top.

Equation Derivation

The rate of change in the cell temperature with time is directly related to the rate of change in the cell power by the equation $dT/dt = (dP/dt)/(dT/dP)$. Therefore, $dT/dt = (dP/dt)/k$ where $k = dP/dT$ with units of W/K. The modeling equation used to define the cell power for this heat conduction calorimeter is

$$P = (E - E_H)I - k(T - T_b) + P_X + P_g + P_W \quad (2)$$

where E_H is the thermoneutral potential defined by $E_H = -\Delta H/2F$ for the cell reaction



For simplicity, the experimental cell voltage and cell current will both be treated as positive quantities for this electrolysis reaction. The P_g and P_W power terms are generally small and can often be ignored.

The derivative of P with respect to time (t) is given by

$$dP/dt = IdE/dt + dP_X/dt - (T - T_b)dk/dt - kdT/dt \quad (4)$$

where I , E_H and T_b are constant. Note that $dP/dt = kdT/dt$. Thus

$$2 dP/dt = IdE/dt + dP_X/dt - (T - T_b)dk/dt \quad (5)$$

or

$$dP/dt = \frac{1}{2} [IdE/dt + dP_X/dt - (T - T_b)dk/dt] \quad (6)$$

The sign for dE/dt and dP_X/dt can be either positive or negative while dk/dt is always negative. Therefore, the term “ $-(T - T_b)dk/dt$ ” will always contribute to a positive value for dP/dt . The calculation of dk/dt can be made using the equation

$$dk/dt = (dk/dV)(dV/dt) \quad (7)$$

where dV/dt is always negative and determined by the cell current. At $I = 0.1500$ A for D_2O electrolysis assuming evaporation is negligible

$$\begin{aligned} dV/dt &= (-0.5 I/F)(20.02784 \text{ g/mol})(1.0 \text{ cm}^3/1.10445\text{g}) \\ &= -1.4096 \times 10^{-5} \text{ cm}^3/\text{s} \end{aligned} \quad (8)$$

The numerical value for dk/dV depends on the cell design and must be determined for each cell by experiments. For the isoperibolic calorimeter used in this experiment, $dk/dV = 2.0 \times 10^{-4} \text{ W/K cm}^3$. Therefore, $dk/dt = -2.82 \times 10^{-9} \text{ W/Ks}$ for this calorimeter when $I = 0.1500 \text{ A}$.

Experimental Verifications

Five data points from two different previous experiments were used to calculate dT/dt values using Equation 6 and the relationship $dT/dt = (dP/dt)/k$. The calculated and experimental dT/dt results are shown in Table 1. A Johnson-Matthey (JM) palladium rod cathode (0.1 x 2.3 cm) was used in the 2016 experiment while a Naval Research Laboratory (NRL) Pd-0.5 B cathode rod (0.47 x 2.0 cm) was used in the 2017 study.

Table 1. Comparisons For Calculated and Experiments dT/dt Results From Two Experiments.

Experiment	I (A)	T – T_b (K)	Calculated dT/dt (K/s)	Experimental dT/dt (K/s)
7/03/2016 JM Pd (3:20 p.m.)	0.0365	0.23	1.41×10^{-4}	1.25×10^{-4}
7/10/2016 JM Pd (11:41 a.m.)	0.2190	9.87	-1.25×10^{-6}	-1.29×10^{-6}
3/18/2017 NRL Pd-0.5 B (6:06 p.m.)	0.1500	0.86	1.32×10^{-4}	1.17×10^{-4}
3/19/2017 NRL Pd-0.5 B (11:08 a.m.)	0.1500	3.16	-7.97×10^{-7} (-0.0029 K/h)	-5.66×10^{-7} (-0.0020 K/h)
3/29/2017 NRL Pd-0.5 B (4:40 p.m.)	0.5000	20.93	-1.18×10^{-6}	-8.85×10^{-6}

Note that in every case, the use of Equation 6 provides the correct sign for the calculation of dT/dt . Furthermore, the numerical values are within the experimental errors expected. Small errors could account for the differences for the calculated and experimental dT/dt values in Table 1, especially for the smaller dT/dt values. For the small dT/dt values in Table 1, even the experimental determination of dT/dt may have rather large errors. In summary, Table 1 supports the use of Equation 6 in the calculation of dT/dt in electrochemical calorimetric experiments. Generally, the experimental dT/dt should be considered as more accurate than the calculated value.

The Measurement of ΔH For D_2O Electrolysis using Electrochemical Calorimetry

Another excellent test of electrochemical calorimetry is the determination of ΔH for the D_2O electrolysis reaction. The calorimetric equation for open isoperibolic calorimetry includes the term $C_p m dT/dt$ (when T_b is constant) as the power for the calorimetric cell (P_{calor}). Therefore

$$C_p M dT/dt = (E - E_H)I - k(T - T_b) + P_X + P_g + P_w \quad (9)$$

where T_b is the constant bath temperature that surrounds the isoperibolic calorimeter. Solving for E_H yields

$$E_H = E - [k(T - T_b) + C_p M dT/dt]/I + (P_X + P_g + P_w)/I \quad (10)$$

The experimental data selected for this determination of E_H was taken between 14 and 29 hours for a cell using a Pt coil anode and a Pd-0.5 B cathode (See 3/19/2017 in Table 1). This was the second day of the experiment where the electrolyte volume was at the correct 50 mL level. Furthermore, the detailed analysis of this data indicated that $C_p M dT/dt \approx 0$ and that $(P_X + P_g + P_w \approx 0)$ during this fifteen-hour time period (See Appendix). Therefore Equation 10 simplifies to

$$E_H = E - k(T - T_b)/I \quad (11)$$

where $I = 0.1500$ A. The $k(T - T_b)/I$ term corrects for the experimental cell voltage being greater than E_H . The data set used to determine E_H must be consistent with the assumption that $P_X = 0$. This is necessary because any calculation of P_X will involve the use of E_H (Equation 9). The calculation of E_H from Equation 11 requires strictly direct experimental measurements (E , I , T , T_b). The cell constants (k) were determined in other experiments using various methods [9-13].

Table 2 presents the experimental cell voltages (E) and calculated values for E_H using the cell and bath temperature measurements for each of the three thermistors. This Table includes every experimental measurement for this second day of electrolysis.

Table 2. Cell Voltage Measurements and E_H Results For Three Cell Thermistors (T_1 , T_2 , T_3).

Time (m)	E (V)	(T_1) E_H (V)	(T_2) E_H (V)	(T_3) E_H (V)
847	4.091	1.544	1.544	1.549
883	4.085	1.551	1.552	1.557
913	4.085	1.555	1.552	1.557
979	4.075	1.545	1.551	1.552
1028	4.055	1.517	1.517	1.513
1093	4.070	1.519	1.523	1.518
1395	4.025	1.483	1.487	1.483
1487	4.050	1.520	1.521	1.517
1570	4.020	1.486	1.491	1.483
1730	4.020	1.498	1.509	1.507
Mean Values For E_H :		1.522	1.525	1.524
		± 0.027	± 0.025	± 0.029

Table 2 suggests that the location of a thermistor was not a major factor as long as accurate calibrations were done. There appears to be a slight decrease in the E_H values with time in Table 2. This may be related to the gradual changes in the cell constants with time during the electrolysis or to the rather low cell voltages that were measured later in this experiment.

The main error source was the cell voltage fluctuations due to gas bubbles forming on the cathode surface. This cell voltage measurement problem due to gas bubbles usually relates to the D₂O bottle and additives used for NMR applications. Generally, the cell voltages can be readily measured to four decimal places in these experiments [8]. This error in cell voltages can be minimized by using the mean E_H value for each thermistor: 1.522 V, 1.525 V and 1.524 V. The mean of these three values yields E_H = 1.5237 V ±0.0015. Therefore, the correct sign convention for ΔH yields

$$\Delta H = 2F E_H = 294.03 \text{ kJ/mol } (\pm 0.29 \text{ kJ}) \quad (12)$$

for D₂O electrolysis (Reaction 3) at the mean cell temperature of 33.34°C (306.49 K). The adjustment of ΔH = 294.03 kJ/mole to the standard temperature (298.15 K) can be made by using the equation

$$\Delta H (T_2) = \Delta H (T_1) + \Delta C_p (T_2 - T_1) \quad (13)$$

where ΔC_p = -40.48 J/mol K for Reaction 3. This correction is + 338 J/mole. Therefore, this experimental enthalpy change for D₂O electrolysis at 298.15 K is

$$\Delta H = 294.4 \text{ kJ/mole } (\pm 0.3 \text{ kJ/mole}) \quad (14)$$

This experimental value obtained by electrochemical calorimetry agrees reasonably well (within 0.10%) with the literature value of ΔH° = 294.600 kJ/mole for Reaction 3 [14]. This value also corresponds to the standard enthalpy of formation (ΔH_f°) for D₂O where ΔH = -ΔH_f for D₂O liquid. This application of electrochemical calorimetry for the determination of ΔH for D₂O electrolysis has not been previously reported. Electrochemical calorimetry research for H₂O electrolysis gave a value of ΔH = 284.4 ±7.4 kJ/mole that is close to the literature value of 285.830 kJ/mole [15]. The present D₂O results and the previous H₂O results [15] both show that no significant degree of recombination was observed in these electrochemical calorimetry experiments. Accurate electrochemical calorimetric methods can provide direct measurements of enthalpies for electrochemical reactions where reversible electrodes are not available [15].

The experimental errors in this study are much larger (±1.7% or ±5.0 kJ/mole) when based upon a single thermistor (Table 2). However, the three different thermistors at different cell locations involving different cell constants could be considered as three separate experiments. The three mean values for E_H in Table 2 differ by only small amounts with a standard deviation of only ±0.00153 or ±0.10%. Therefore, the standard deviation for ΔH = 294.4 kJ/mole is ±0.3 kJ/mole. The experimental data for the third day of electrolysis gave similar results with ΔH = 294.3 kJ/mole at the mean cell temperature of 33.27°C or 294.6 kJ/mole at 25.0°C. The only changes in the calculations were slightly smaller cell constants using dk/dt = -2.82 x 10⁻⁹ W/Ks from Equation 7.

It is reported that ΔH_f° = -249.2032 kJ/mol for D₂O gas [14]. Combining this value with ΔH° = -45.401 kJ/mol for converting the gas to a liquid gives ΔH_f° = -294.604 kJ/mol for D₂O liquid.

Summary

Electrochemical calorimetry can be accurate if the correct equations are used. The application of Equation 6 leads to calculated changes of the cell temperature with time (dT/dt) that agree reasonably well with experimental measurements. The application of Equation 11 yields the enthalpy change (ΔH) for D_2O electrolysis that is close to the reported value from other methods. The position of the thermistor within the calorimeter is not a major factor if accurate calibrations are done. There was no evidence for any reactions involving D_2 and O_2 gases in these experiments nor were there any significant excess power effects (P_x) during the time period investigated for the enthalpy of the D_2O electrolysis reaction.

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Appendix

All experimental thermistor readings for this study are presented in Table 3. Thermistor T₁ was in the cell electrolyte, thermistor T₂ was on the outer wall of the cell, thermistors T₃ and T₄ were in the constant temperature water bath, and thermistor T₅ was opposite T₂ on the outer cell wall. These thermistor readings were accurate to about ±0.005 K.

Table 3. Thermistor Temperatures For The Cell (T₁, T₂, T₅) and Bath (T₃, T₄).

Time (m)	T1 (°C)	T2 (°C)	T3 (°C)	T4 (°C)	T5 (°C)
847	33.360	32.890	29.810	30.250	32.730
883	33.355	32.885	29.820	30.260	32.725
913	33.350	32.885	29.820	30.260	32.725
979	33.350	32.875	29.820	30.260	32.720
1028	33.350	32.885	29.815	30.250	32.730
1093	33.365	32.890	29.810	30.250	32.740
1395	33.335	32.860	29.790	30.230	32.710
1487	33.320	32.850	29.790	30.230	32.700
1570	33.315	32.840	29.780	30.220	32.695
1730	33.310	32.850	29.790	30.230	32.680

$$\Delta T_1 = T_1 + 0.06 - T_4 \quad , \quad k_1 = 0.1205 \text{ W/K}$$

$$\Delta T_2 = T_2 - 0.25 - T_3 \quad , \quad k_2 = 0.1350 \text{ W/K}$$

$$\Delta T_5 = T_5 + 0.15 - T_4 \quad , \quad k_5 = 0.1450 \text{ W/K}$$

Thermistors T₁ and T₅ were calibrated against T₄ while thermistor T₂ was calibrated against T₃. It is only the temperature differences, T – T_b, that enters into these calculations in Equation 11.

All the results for E_H presented in Table 2 can be checked by Equation 11 using the cell voltages in Table 2 and the temperature data and cell constants given in Table 3. Furthermore, for Equation 6, dE/dt obtained from Table 2 is -1.34×10^{-6} V/s and $dk/dt = -2.82 \times 10^{-9}$ W/Ks from Equation 7.

The two terms, $C_p M dT/dt$ and the sum of $P_X + P_g + P_W$ that were assumed to be zero in Equation 10 can actually be evaluated from the experimental results shown in Tables 2 and 3. The cell and bath temperatures using thermistors 1 and 4 in Table 3 yield $dT/dt = -5.66 \times 10^{-7}$ K/s. Therefore, $C_p M dT/dt = -0.000255$ W. The sum of $P_X + P_g + P_W$ obtained using Equation 9 with $E_H = 1.5267$ V was 0.78 ± 3.99 mW for thermistor T_1 , 0.59 ± 3.94 mW for T_2 and 0.50 ± 4.34 mW for T_5 . The mean value from all three cell thermistors was

$$P_X + P_g + P_W = 0.00062 \text{ W} \quad (\text{A.1})$$

These calculations show that both $C_p M dT/dt$ and the sum of $P_X + P_g + P_W$ are small power terms that can be assumed to be zero (within experimental errors) for the data presented in Tables 2 and 3.

The small P_g and P_W terms can also be calculated for this data set independently of E_H using the following equations [6-8,12].

$$P_g = - (I/F) [0.5 C_{p,D_2} + 0.25 C_{p,O_2} + 0.75 P' C_{p,D_2O}] \Delta T - 0.75 (I/F) P' L \quad (\text{A.2})$$

where $P' = P/(P^* - P)$, P is the vapor pressure of D_2O at the cell temperature and P^* is the atmospheric pressure in the laboratory. The heat capacities (C_p) are for the gases leaving the cell (D_2 , O_2 , D_2O) while $\Delta T = T - T_b$. The second term involves the enthalpy of evaporation (L) for D_2O . The P_W term for expansion work is simpler and given by

$$P_W = -RT (0.75 I/F) \quad (\text{A.3})$$

using the perfect gas equation for the 0.75 moles of $D_2 + O_2$ electrolysis gases generated per Faraday [12].

The mean cell temperature used in these calculations was $T = 33.27^\circ\text{C} = 306.42$ K while the laboratory pressure was $P^* = 700$ Torr (elevation 765 m). The use of these equations yields $P_g = -0.00260$ W and $P_W = -0.00396$ W.

The purity of D_2O could also affect the experimental ΔH value for D_2O electrolysis. At the stated 99.9% D, the effect on ΔH would be insignificant at -11 J/mole. However, at 99.0% D, the ΔH value would be lowered by -102 J/mole. One important advantage of open electrochemical cells is that any H_2O contamination will be preferentially removed by the electrolysis.