CALORIMETRY OF OPEN ELECTROCHEMICAL CELLS.

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ABSTRACT

A special case of calorimetry of open electrochemical cells, that employing adiabatic enclosures, **is** examined. Conditions for an experimental realization of such enclosures is discussed in detail. Practical arrangement and method for data collection are presented.

1.0   INTRODUCTION

Following the announcement by Fleischmann and Pons(1) that anomalous effects, among them excess heat generation, can be observed when deuterium is electrochemically compressed in the Pd-lattice, the discussion of the calorimetry of open electrochemical cells became of considerable interest. **A** calorimeter is an apparatus designed to measure quantities of heat associated with the occurrence of specific processes (eg, heatof reaction, heat of absorption, etc.) or the property of matter (eg, specific heat). The basis for such measurements is the conservation of energy and requires knowledge of the process(es) under consideration, the sequence of events, the construction of the apparatus and the experimental procedure employed. In other words, the development of the calorimetric equation for an operating electrochemical cell employs conservation of energy and adjusts the applicable walls and constraints in a manner consistent with cell design and relevant experimental procedure(s).

2.0   PROCESSES IN OPEN ELECTROCHEMICAL CELLS

In the simplest arrangement, an electrochemical cell is a three phase, multi-component assembly wherein the charge transfer reaction(s) and associated transport processes occur. Initially, this system is in thermal, mechanical and chemical equilibrium. Upon initiation of current flow, significant changes in temperature and concentration take place, viz., the development of gradients which, in turn, initiate transport processes in the electrolyte phase and across the electrolyte/gas interface. The increase in the temperature arises from the irreversible processes: the joule heating, the electrodic processes and the exothermic absorption of deuterium by the palladium electrode as well as due to the exchange with the environment. In the absence of the electrolyte stirring, temperature and concentration gradients promote the development of convective flow. If the convective flow is sufficiently intense, it results in a uniform composition and temperature distributions throughout the electrolyte phase.

With the initiation of current flow, not only the equilibrium is disturbed but both the composition and temperature change with time. In particular, the removal of water from the electrolyte is by electrolysis and vaporization. These processes reduce the electrolyte volume by $dV^{(1)}$ while the volume of the gas phase is increased by $dV^{(2)}$, their sum being calculated from the quantity of charge transferred, faradaic efficiency and the gas laws. A constant pressure can be maintained by adjusting (reversibly) the position of a piston or allowing the outflow of gas from the cell head space. (Note: thermal effects associated with the change in the electrolyte composition due to water removal, are neglected).

3.0   CONSERVATION OF ENERGY

Equilibrium state in any system is completely characterized by the internal energy, U, the volume, V, and the mole number, nj, of chemical components, ie, $U = U(T, V, n_j)$, of which the first differential is

$$dU = \frac{\partial U}{\partial T}\bigg|_{V,n_j} dT + \frac{\partial U}{\partial V}\bigg|_{T,n_j} dV + \sum_j \frac{\partial U}{\partial n_j}\bigg|_{T,V} dn_j \tag{1}$$

where: $\frac{\partial U}{\partial V}\big|_{t,n_j} = -p;\frac{\partial U}{\partial n_j}\big|_{T,V} = \mu_j$ are the intensive parameters. In the energy representation, the independent variables are the extensive properties with the intensive properties as derived quantities.. If a constant pressure processes are examined, the use of the enthalpy function is more convenient. In the enthalpy representation, the pressure is substituted for volume, ie, H = H(T, p, n$_j$). Both quantities, U and H, are unambiguously defined in closed and open systems because the changes in state variables are independent of whether the change in composition, dnj, is due to an exchange or chemical reaction. Consequently, in open systems, the only valid statements are:

$$U = \sum U^a \ ; \ H = \sum H^a \ ; \ H^a = U^a - \sum_j L_j^a l_j^a \ ; \ \alpha = 1,2,...; j = 1,2,...$$

while terms "work" and "heat" are ambiguous. The ambiguity is removed. however, if we define work and heat by

Eqs. (2) and (3) respectively

$$dW = \sum_j L_j dl_j + dW_{diss} + dW_a \tag{2}$$

and

$$dQ = dU - dW - \sum_k \frac{\partial U}{\partial T}\bigg|_{V,n_j} dT + Vdp + \sum_j \frac{\partial U}{\partial n_j}\bigg|_{T,V} dn_j \tag{3}$$

and, if it is understood that dW measures the work that would have been done if the system under consideration were closed(2,3).

While the infinitesimal change in the internal energy is given by Eq. (1), the change in the enthalpy (H = U + pV), is given by Eq. (4)

$$dH = \frac{\partial U}{\partial T}\bigg|_{V,n_j} dT + Vdp + \sum_j \frac{\partial U}{\partial n_j}\bigg|_{T,V} dn_j \tag{4}$$

which, at p = const., because of the equality $\frac{\partial U}{\partial n_j}\big|_{T,V} = \frac{\partial H}{\partial n_j}\big|_{p,T} = \mu_j$ becomes Eq. (5)

$$dH(T, n_j) = \frac{\partial H}{\partial T}\bigg|_{n_j} dT + \sum_j \frac{\partial H}{\partial n_j}\bigg|_T dn_j \tag{5}$$

4.0 FORMULATION OF CALORIMETRIC EQUATION

In deriving the calorimetric equation, we balance the change in the enthalpy of the electrolyte phase with the enthalpy gain or loss attributed to the participating processes. In particular, applying the enthalpy balance to an open electrochemical system (not including cell walls and electrodes), illustrated in Fig. 1, we obtain, with dn$_j$ <0

$$\frac{\partial H^{(1)}}{\partial T}\bigg|_{n_j} dT - \sum_j \frac{\partial H^{(1)}}{\partial n_j}\bigg|_T dn_j = dH* - dw + \sum dH^{(1 \to v)} + \sum dH^{(1 \to e)} \tag{6}$$

where dH* is the energy produced (excess enthalpy), dw is the work done on the surroundings, $\sum dH^{(1\to v)}$ is the enthalpy transferred between the electrolyte and gaseous phases and $\sum dH^{(1\to e)}$ is the enthalpytransferred to or from the environment. The direction of transfer determines the sign, viz., the quantity removed from the system is negative. As written, the left side of Eq. (6) denotes change in the enthalpy that is measured. The right hand side contains contributions attributed to known as well as unknown processes, including the term representing an excess of enthalpy. The corresponding change in the gas phase is

$$\frac{\partial H^{(v)}}{\partial T}\Big|_{n_j} dT + \frac{\partial H^{(v)}}{\partial n_j}\Big|_T dn_j = \sum dH_j^{(1\to v)} + \sum dH_j^{(1\to e)} \tag{6a}$$

In formulating the calorimetric equation, only the rate of the enthalpy change in the electrolyte phase is considered. By dividing each term of Eq. (6) by dt, and identifying participating processes, we obtain the governing differential equation, Eq. (7)

$$\frac{\partial H^{(1)}}{\partial T}\cdot\frac{dT}{dt} - \sum_j \frac{\partial H^{(1)}}{\partial n_j}\cdot\frac{dn_j}{dt} = J^* + I(E_c - E_{th}) + \sum_j J^{(1\to 2)} + \sum_j J^{(1\to e)} \tag{7}$$

The information sought to confirm the initiation of the F.-P. effect, is the numerical value of the first term on the right hand side, J*. (For completeness, the J* term includes also thermal effects arising from the interaction between the adsorbed-absorbed deuterium and palladium lattice.)

5.0 REMARKS CONCERNING THE OPEN CELL CALORIMETRY

The solution of Eq. (7) requires specification of the initial conditions and evaluation of all other terms consistent with the mode of operation and cell design. The initial conditions are the equilibrium conditions, ie, the temperature of the whole system is that of the environment and the composition of gas phase is $D_2 : O_2 = 2:1$ with the D_2O vapor in equilibrium with the electrolyte. The rate of heat transfer out of the cell depends on the cell geometry, construction of the enclosure and mode of transport. The simplest case is that of an adiabatic wall. If, however, the enclosure is a diathermal wall, then the heat transfer may occur either via radiation with some convective contributions or via convection with minor radiative contributions.

The criticism of the open cell calorimetry is centered around the assumption of a steady state heat transport to the environment and the selected calibration procedure. To assure correct interpretation of thermal behavior of the electrolyte phase it is necessary to know the rate controlling process, its temperature dependence and relaxation time. The concept of the relaxation time is well defined in thermodynamics, viz., the relaxation timeexpressed in terms of variable, $\xi(t)$, is the decrease of its value to the equilibrium (or the steady state) value, ξ_{eq}. The approach to the equilibrium follows an exponential law $\xi(t) = \xi_{eq} + Ce^{\frac{t}{\tau}}$ where C is the integration constant and τ is the relaxation time. The temperature dependence of the terms in Eq. (6/7) is discussed below.

5.1 Heat Content of the Electrolyte Phase

As written, the first term on the left hand side represents the rate of change in the heat content of the electrolyte as a function of time, evaluated at temperature T(t). Assuming a 100% faradaic efficiency, the consumption of solvent equivalent, $s = D_2O$, in a cell operating for time t seconds at the current density, I amperes, is: $It/2\mathbf{F}$, so that the rate of change in the electrolyte heat content is

$m_o c_s\left(1 - \frac{It}{2Fm_o}\right)$ where m_0 is the initial amount of solvent.

5.2 Electrical Work, dw

An unique feature of an electrochemical cell is the occurrence of charge transfer reaction(s) whereby electrons generated at the negative are transferred in an external circuit and consumed at the positive electrode in another charge transfer reaction. In a steady state, the number of electrons leaving and entering the cell is the same which means that the electrochemical cell can be considered a closed system with regard to the electrical charge (potential difference build up occurs at the phase boundary only). Irrespective of the direction of current flow, the product, IE_c, must be a positive quantity. By convention, the positive current is flowing out of the cell, so that the electrical work term in Eq. (7) is positive. The enthalpy input to the cell, expressed as an electrical work and corrected for the recoverable enthalpy is $I(E_c - E_{th})dt$, where $E_{th} = -\Delta H/zF$ is the thermoneutral potential.

5.3 Rate of enthalpy transfer, $J^{(1 \to v)}$, $J^{(1 \to e)}$

In the system under consideration, the $J^{(1 \to v)}$ – term represents the sum of the enthalpy carried out by the rising gas bubbles, saturated with D_2O vapor at the cell temperature and that due to the phase change: $D_2O(s) \to D_2O(v)$. The respective rates are: $\dfrac{I}{F}\left[\dfrac{1}{2}c^{(v)}_{D_2} + \dfrac{1}{4}c^{(v)}_{o_2} + \dfrac{3}{4}\dfrac{p}{p*-p}c_{s,g} \right]$ and

$\dfrac{3}{4}\dfrac{I}{F}\dfrac{p}{p*-p} \cdot L^{(1 \to v)}$.

Parenthetically, we note that excluding chemical reaction(s) in either system and the energy transfer from the enviroment, we have for the mass balance and mass flux, Eq. (8)

$$dn^{(1)}_k + dn^{(2)}_k = 0; J_m = dn^{(1)}/dt = -dn^{(2)}/dt \tag{8}$$

and for the enthalpy transfer, Eq. (9)

$$\left[dq^{(1)} + \sum_k \left(\frac{\partial H}{\partial n} dn \right)^{(1)} \right] + \left[dq^{(2)} + \sum_k \left(\frac{\partial H}{\partial n} dn \right)^{(2)} \right] = 0 \tag{9}$$

from which the heat flux, $J^{J(1 \to 2)}_q$, is given by equation

$$J^{(1 \to 2)}_q = -\sum_k \frac{\partial H}{\partial n} \cdot J^{(1 \to 2)}_m \tag{10}$$

Equation (10) states that the equality: $dq^{(1)} = dq^{(2)}$ can occur only in the absence of mass transport. The $J^{(1 \to e)}_q$– term is, as a rule, of the form of the generalized Ohm's law, ie. $J^{(1 \to e)}_q = k(T^{(1)} - T^{(e)})$, where k is usually taken to be a constant within the temperature range $(T^{(1)} - T^{(e)})$. Its numerical value depends upon the composition of the wall with the applicable computation methodology described in textbooks on heat transfer.

5.5 Temperature Dependent Parameters

Excluding the J*– term, all terms on the right hand side of Eq. (7) are temperature dependent in a simple way except for the $I(E_c - E_{th})$– term. The temperature dependence of the specific heat is usually taken as a linear function of temperature. The term, accounting for the enthalpy transport to the vapor phase, consists of two parts: $J_1(I, T)^{(1 \to v)}$ and $J_2(p*, T)^{(1 \to v)}$ of which $J^{(1 \to e)}_1$ identifies the small amount of heavy water evaporating into the D_2 and O_2 gas bubbles. This term is a function of the cell current and temperature and is negligible, except at higher solution temperatures and current densities. The second contribution, $J^{(1 \to e)}_2$ denotes the loss of water due to evaporation. The rate of

evaporation is proportional to the solution temperature and as the solution temperature approaches the boiling point, the $J_2^{(1\rightarrow e)}$– term dominates. The p(T) dependence is calculated using the ClausiusCla-peyron formula, $dp/dT = L/T[v^{(g)} - v^{(s)}]$. The contribution $J_2^{(1\rightarrow e)}$ can be evaluated quite easily, but not the $J_1^{(1\rightarrow e)}$ because of a number of factors must be considered, among them the size of gas bubbles, the degree of their saturation, etc.

Less clear is the temperature dependence of the term $I(E_c - E_{th})$. Employing the procedure adapted by Pons and Fleischmann(6), the correction factor is

$$\psi = \left\{ \frac{dE_c}{dT} + \frac{3}{4\mathbf{F}} \cdot \frac{d}{dT}\left[\frac{p}{p*-p}(c_s^{(v)}\Delta T + L^{(1\rightarrow v)}) \right] \right\}\Delta T.$$

This procedure involves expanding the temperature dependent $(E_c - E_{th})$ term into the Taylor series, retaining the first term only on account of smallness of ΔT and expressing E_{th} by the change in the enthalpy function of the electrolyte due to the increase by ΔT. It is noted that, if a chemical (electro-chemical) reaction occurs at a constant pressure and temperature, the heat of reaction is the change in enthalpy while the change in mole number is the change in the Gibbs function.

5.6   Complete Calorimetric Equation

The expression for a complete energy/mass balance is obtained upon integration of

$$\left[\sum m_i c_i \frac{dT}{dt} \right] + m_o c_s \left(1 - \frac{It}{2m_0\mathbf{F}} \right)\frac{dT}{dt} - \frac{c_s IT}{2\mathbf{F}} = J* + I(E_c - E_{th} + psi) + \sum J^{(1\rightarrow 2)} + \sum J^{(1-.e)} \tag{11}$$

where the first term accounts for the contribution of all cell components except the electrolyte. This term must be carefully evaluated during the course of long term experiments and, in particular, during the calibration procedure because the relaxation time is strongly affected by the physico-chemical properties of walls and enclosures. Note: henceforth superscript (2) is employed to identify the bath **as** separate from the environment.)

6.0.   CALORIMETER DESIGN AND MODELING

Consider a system consisting of an electrochemical cell containing a known amount of electrolyte and totally immersed in a water bath. Initially, this system is in equilibrium and, for the duration of an experiment, the bath is in contact with an infinite heat sink. (ie, $T^{(e)}$ = const). Applying the conservation of energy, in the form of condensed Eq. (6/7), the rate of the temperature change with time in the cell, after its activation, is

$$C_1\frac{dT_1}{dt} = Q_1 - J_q^{(1\rightarrow 2)} - J_q^{(1\rightarrow 3)} \tag{12}$$

and in the water bath

$$C_2\frac{dT_2}{dt} = Q_2 + J_q^{(1\rightarrow 2)} - J_q^{(2\rightarrow e)} \tag{13}$$

where $C_1 = \Sigma m_{1,i} c_{1,i}$ is the heat capacity of the electrolyte and includes all cell components (cell constant), C_2 is the heat capacity of the bath fluid, $Q_l = [J* + I(E_c - E_{th})]$ denotes the rate of heat production in the electrolyte phase, Q_2 is the heat supplied to the bath in order to maintain $T^{(1)} = T^{(2)}$, and the J's are the heat fluxes exchanged between system elements, viz., the electrolyte, bath and environment.

6.1 Construction of an Adiabatic Wall

Equation (12) is the energy balance expressed in terms of the rate of heat generation due to the irreversibilities of the charge transfer process(es), the rate of heat exchange between the cell and the water bath, and the rate of heat loss to the environment. Since the term, Q_1 is always positive, it follows that $T^{(1)} > T^{(2)}$ resulting in an outflow of heat generated within the cell. The construction of an adiabatic wall requires that $J_q^{(1 \to e)} = J_q^{(2 \to 1)} = 0$ at all times. This requirement is fulfilled as long as $\Delta T = T^{(1)} - T^{(2)} = 0$, ie, as long as $J_q^{(2 \to e)} = Q_2 - C_2(Q_1 - J_q^{(1 \to e)})/C_1$ which, for $Q_1 >> J_q^{(1 \to e)}$, is further simplified to $J_q^{(2 \to e)} = Q_2 - C_2 Q_1/C_2$ and provides a rough guide for design and operation of an adiabatic wall separating the cell from bath. In practice, $\Delta T \neq 0$; consequently, the maintanence of an adiabatic wall requires that $\int_t J^{(1 \to 2)} dt = \int_t J^{(2 \to 1)} dt$ ie, that ΔT oscillates about its zero value.

Employing, for thermal flux, an expression of the form $J = k\Delta T$ and introducing a new set of variables, viz., $\Delta T = T^{(1)} - T^{(2)}$ and $= T^{(1)} - T^{(e)}$ with $T^{(e)}$ — const , Eq. (12) becomes Eq. (14)

$$\frac{d\theta}{dt} = q_1 - k_{12}\Delta T - k_{le}\theta \tag{14}$$

Using the same variables, by subtracting Eq. (13) from (12), we obtain an expression for the change in T, Eq. (15)

$$\frac{d\Delta T}{dt} = (1_1 - q_2) - (k_{12} + k_{12}^* + k_{2e})\Delta T + (k_{2e}0k_{1e})\theta \tag{15}$$

where $q_i = Q_i/C_i$; $k_i = k_i/C_i$ and $k^* = k_{12}/C_2 = k_{12}C_1/C_2$. Conditions forcing ΔT to oscillate about zero can be determined by solving the set of coupled differential equations, Eqs. (14) and (15).

To maintain an adiabatic wall, the positive ΔT due to $q_1 > 0$ must be countered by q_2 to reverse the direction of heat flow, Eq. (15). One way to construct and maintain an adiabatic wall is as follows: At $t < t_0$, the system is in equilibrium. At t_0 the flow of cell current is initiated causing the system's temperatures to rise (cf. Eq. (14)), as schematically shown in Fig. 2 by solid, $T^{(1)}$, and dashed, $T^{(2)}$, lines. At t_1 the difference ΔT reaches an a priori specified value, and the heat source in the bath, q_2, is activated. If $q_2 > q_1$, then the temperature $T^{(2)}$-rises faster than $T^{(1)}$, in time—at t_2—reducing ΔT to zero. Within this time period there is net heat flow from the cell to the bath. To maintain an adiabatic wall it is necessary to transfer the same amount of heat from bath to cell ($H^{(1 \to 2)} = H^{(2 \to 1)}$) by activating the q_2 and operating it for a required time period. These periods are determined by numerically solving Eqs. (14) and (15).

Some useful information concerning the form of the $\Delta T(t)$ function can be derived if the cell temperature, θ, is considered a constant. Rewriting Eq. (15) in an equivalent form, Eq. (16)

$$\frac{d\Delta T}{a - b\Delta T} = dt \tag{16}$$

where $a = (q_1 - q_2) + (k_{2e} - k_{1e})$ and $b = (k_{12} + k^*_{12} + k_{2e})$, we obtain, upon integration Eqs. (17) and (18) for $q_2 = 0$ and for $q_2 > q_1 + (k_{2e} - k_{1e})\theta$, respectively.

$$\Delta T(t) = \frac{a}{b} + \left[\frac{a}{b} - \Delta T(0)\right]e^{=b(t - t(0))} \tag{17}$$

$$\Delta T(t) = -\frac{a}{b} + \left[\frac{a}{b} - \Delta T(0)\right]e^{-b(t - t(0))} \tag{18}$$

Evidently, the system relaxes with the characteristic time constant $= 1/(k_{12} + k^*_{12} + k_2e)$; That is, the relaxation time is governed by the C_1/C_2 ratio, the cell temperature, materials of construction and the system's contact with the environment. For any selected $\Delta T^{(1)}$ there is a corresponding $\Delta T^{(2)}$ which assures that $(H^{(1 \to 2)} = H^{(2 \to 1)})$ is real- ized. For all practical purposes, this condition is satisfied by the requirement that $\Delta T(t)$ oscillates about zero.

6.2   Temperature Tracking

In any implementation of a calorimeter based on equations (14) and (15), a means of controlling the heat input to the bath surrounding the reaction cell must be provided so as to maintain the temperature difference, $\Delta T = 0$, or, at least, so that it averages to zero over an experimental run. Because of the large amount of temperature data required for an experiment, digital acquisition of the data is necessary; consequently, digitai control of the experiment is a natural choice. In a digital system, the relevant temperature measurements are madein sequence in a repetitive cycle, with some dead time for writing data to a disk and the analog values are to the precision of the analog-to-digital converter being used. These two procedures should not be considered independently because often the truncation error exceeds the allowable temperature error and appropriate averaging is required In order for averaging to improve a measurement, the analog signal must be dithered, either deliberately or by noise over a range corresponding to the least significant bit of the digitized signal. For example, with a twelve-bit analog-to-digital converter having an input of $–20$ to $+20$ mV, the least significant bit corresponds to a 10 μV input signal change or a change 0.25 C for a T-type thermocouple where the sensitivity is about 25 mC/μV. Typically, there might be present 10 μV rms noise referred to the input, so that averaging 100 samples would be expected to reduce the error to about 0.03 C without having to dither the input. Averaging 100 samples has other implications, however, since the averaging takes place over a range of temperature difference, ΔT , that depends on both, the cooling rate of the cell and the heating rate of the bath as given by Eqs. (14,15). On average, a temperature offset occurs that depends on whether T takes longer to recover from a positive value than from a negative value, which would increase the likelihood that the bath heater will be incorrectly turned on rather than incorrectly turned off. These effects exhibit temperature dependence that can be demonstrated in modeling the calorimeter by introducing truncation and noise into the test as to whether the heater should be on or off.

6.3   Calorimetry of Co-Deposition Process

The codeposition process is the process where the electroreduction of Pd^{2+} ions occurs simultaneously with the evolution of deuterium. The principal advantage of this technique is elimination of the prolonged charging time required for, and a better reproducibility of, the initiation of the Fleischmann–Pons effect. The codeposition process modifies somewhat the calorimetric equation, Eq. (7), making its interpretation less clear. The modification involves the $I(E_c - E_{th})$ term. The cell current is split into two currents, viz., I_1, representing the rate of Pd^{2+} ion reduction and I_2 participating in the reduction of heavy water. The division of currents is potential and time dependent(6). However, as the concentration of Pd^{2+} becomes less, the I_2 current increases and, upon compilation of the codeposition, being equal to the cell current.

An example of thermal behavior during the codeposition process is illustrated in Fig. 3, where excess enthalpy is plotted against the energy supplied to the cell from an external source. During data collection the cell was isolated from the environment by adiabatic wall constructed in manner described above. Clearly, during the initial period, considerable portion of the total current was used up to reduce the Pd^{2+} ions, resulting in the negative excess enthalpy. However, with the passage of time, as I_1 became less, an excess enthalpy. was measured. The. rate of production was not uniform,

ie showing occasional small bursts, and, in general, became higher with an increase in cell temperature.

This example is included to demonstrate that useful information concerning thermal behavior of open cells can be obtained without elaborate instrumentation. Further discussion is outside of the scope of this communication and will be given elsewhere.

7.0 SUMMARY

A discussion of thermal behavior of open electrochemical cells employed to confirm and examine the Fleischmann–Pons effect for a special case of electrodes prepared by codeposition in is presented. The calorimetric equation, written in the enthalpy representation, contains statements of energy/mass conservation, accounts for participating processes and examines the relaxation times. Conditions for construction and data collection in the case of adiabatic enclosure are given. An example of the thermal behavior of the Pd/D system prepared by the codeposition technique showing substantial production of excess enthalpy is included.

Symbols

c - specific heat

C - cell constant, intergration constant

e - environment

F - Faraday constant

E - cell potential, V

H - enthalpy, $Jmol^{-1}$

I - cell current, A

j - running index

J - flux,

J* - rate of excess enthalpy production

k - coefficient

L - work coefficient, latent heat of vaporization

l - work coordinate

n - mole number

m - mass

p - pressure

Q - heat

q - heat source

s - superscript/subscript refers to solvent

T - temperature, K

U - internal energy

V - volume

W - work

α - phase (superscript)

$k = k_i/C_i$ - coefficient

$\theta = T^{(1)} — T^{(e)}$ temperature

μ - chemical potential

τ - relaxation time

ζ - variable

References

1. 1. M. Fleischmann and S. Pons, J. Electroanal. Chem., **261**, 301(1989)

2. 2.H.B. Callen, **Thermodynamics,** John Wiley & Sons, Inc., **New** York – London - Sydney, 1966

3. **3.** R. Haase, **Thermodynamics of Irreversible Processes,** Addison-Wesley Publishing Co, Inc., Reading - Menlo Park-London, 1969

4. 4. P. Van Rysselberghe, in **Modern Aspects of Electrochemistry,** Vol. 4, J.O'M. Bockris and B.E. Conway, eds., Plenum Press, New York, 1966

5. 5. SR. de Groot, **Thermodynamics of Irreversible Processes,** North-Holland Publishing **Co,** Amsterdam, 1952

6. 6. S. Szpak, P.A. Mosier–Boss and J.J. Smith, J. Electroanal. Chem., in the press

Figure captions

Fig. 1 -Thermodynamic boundary for open electrochemical cell system.

The J's represent the rate of enthalpy transfer across boundary (system walls) indicated by the super-script

Fig. 2 -Temperature tracking to maintain an adiabatic wall ($1 \rightarrow 2$).

$\Delta T^{(1)}$ and $\Delta T^{(2)}$ are the temperature differences that trigger (on/off) the heat source in the bath

Fig. 3 - Excess enthalpy generated in the course of Pd/D codeposition from LiCl containing electrolyte.

Figure with x-axis "Apparent Total Energy, IE$_C$" (×10^4) ranging from -0.02 to 1.25, and y-axis "Excess Energy, Q-I (E$_C$ - E$_{mV \times 10^3}$)" (×10^3) ranging from -0.25 to 3.53.