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ELECTROLYSIS IN CALORIMETRY

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The procedure used by many electrochemists in calculating enthalpy in calorimetric measurements of electrolysis reactions is compared to a purely thermodynamic approach, using the data published by Fleischmann *et al.* [J. Electroanal. Chem., 287 (1990) 293.] as a case study.

The set of excess values $d\Delta H_{ex}/dt = d\Delta H_{obs}/dt - d\Delta H_{cal}/dt$ obtained with the former procedure was neither correlated to any of the experimental parameters nor to the set of values found using thermodynamics. The latter, smaller by factors of up to two orders of magnitude, are shown to follow an expression of the form $d\Delta H_{ex}/dt = -kI \exp(-E_a/RT)$ with an activation enthalpy of about 85 kJ·mol^{-1}. It is suggested that recombination of electrolysis gases may account for this.

Keywords: calculation of enthalpy, calorimetry, electrolysis

Introduction

Recently the results of an extensive calorimetric study of the electrolysis of heavy water with palladium cathodes over long ($>10^6$s) periods of time were published by Fleischmann and coworkers [1]. With a heat-flow calorimeter they measured steady state values of voltage, current and temperature in more than fifty cases. Their calculations involve a complex of more than 60 equations but apparently make no use of known standard enthalpies such as that of formation of heavy water. Estimates of error associated with the method are not given.

The present paper takes the experimental data of Ref. [1], calculates the rate of change of enthalpy using simple thermodynamics, and compares it with accepted enthalpy values. The resulting excess values do not correlate with those of Ref. [1], being smaller by factors of 2 to 100. In contrast to the latter they were shown to depend linearly on the electrolysis current and on an Arrhenius factor over the full range of measurement.

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Comments on the calculations by Fleischmann et al.

Appendix 3 of Ref. [1], to which most remarks in this section apply, contains a list of the contributions to the enthalpy balance set up by Fleischmann *et al.*, with an overview given in Fig. A3.1. They are not all correct, and the treatment of data is open to criticism.

The expressions (A3.4) and (A3.2), which contain heat capacities of reactant and products, respectively, imply that the reactant is heated from the temperature of the 'make-up' (deuterium oxide refill) stream to that of the cell, and that the products are cooled from the cell temperature to that of the bath. Neither describes the actual practice: deuterium oxide is at cell temperature when measurements are taken (as noted p. 332), and the products leave the cell at cell temperature.

Equation (A3.5) gives the number of moles of deuterium oxide in the cell whereas the 'water equivalent' needed here is the total heat capacity of the liquid, of the solids immersed in it, and of the inner wall of the Dewar in contact with it.

More important, and less transparent, is the way in which the excess enthalpy is calculated. It appears for the first time in Eq. (A3.1) and is later Eq. (A3.9) replaced by $E_{\mathrm{thermoneutral.bath}}$ which is a constituent of β_1 (A5.5), one of five parameters ultimately determined by fitting Eq. (A5.10) to experimental data.

This indirect way of calculating the excess enthalpy without using independent data for comparison, e.g. obtained by combustion calorimetry, intuitively appears dangerous. Below, an alternative method is described which is wholly consistent with thermodynamics, and which uses tabulated data for comparison.

Alternative enthalpy–balance equation

The method adopted here was described in a recent publication [2]. Let the system be defined as the calorimeter vessel (inner Dewar wall) plus its contents, and let the pressure be constant. With a change of independent variables from the set $\{S, p, n_{\mathrm{B}}\}$ to $\{T, p, n_{\mathrm{B}}\}$, the system enthalpy differential becomes

$$\mathrm{d}H = C_{\mathrm{p}}\mathrm{d}T + V(1-\alpha T)\mathrm{d}p + \sum_{B} H_{\mathrm{B}}\,\mathrm{d}n_{\mathrm{B}} = \delta W' + \delta Q \tag{1}$$

where α is the volume coefficient of thermal expansion of the system, and $\delta W' + \delta Q$ stands for the useful work (including electric work supplied in electrolysis) and heat transferred to the system. Because of the assumption of steady state and constant pressure the first two terms of the central expression vanish. Dividing by δt we get

$$\sum_{B} H_{B} \frac{dn_{B}}{dt} = P + \Phi \tag{2}$$

where P is the electric power delivered and Φ the heat flow transferred to the calorimeter. The LHS of Eq. (2) may be calculated for processes known to take place in the calorimeter while its RHS, accessible experimentally, is a measure of the factual enthalpy rate of change. Comparison may reveal the presence of possible reactions not taken into account.

Terms in the enthalpy - balance equation

a1) The electric power P is given as the product of the terminal voltage U with the total current through the cell I,

$$P = U \cdot I \tag{3}$$

a2) The heat flow to the vessel is the sum of two terms due to conduction and radiation, Eq. (A2.1) in Ref. [1],

$$\Phi = -k_{c}\Delta T - k_{r}(T^{4} - T_{\mathrm{bath}}^{4}) \tag{4}$$

where T and T_{bath} are the temperatures of the cell and bath respectively, $\Delta T = T\text{-}T_{\mathrm{bath}}$, k_{c} is the thermal conductance, and the last term gives the radiant power. If a Taylor expansion of T^{4} around T_{bath} is made, and terms of the third degree and higher are neglected, the expression may be written

$$\Phi = -\left[k_{c} + 4k_{r}T_{\mathrm{bath}}^{3}(1 + 1.5\Delta T/T_{\mathrm{bath}})\right]\Delta T \tag{5}$$

b1) The main enthalpy change comes from the reaction

$$(r) \qquad D_2O(l,T) \xrightarrow{2F} D_2(g,T,p_{D_2}) + \tfrac{1}{2}\,O_2(g,T,p_{O_2}) \tag{6}$$

If the molar enthalpy is $\Delta_{r}H_{m}$, the extent ξ_{r} and the current yield $\gamma = 1$ (p. 301 in Ref. [1]), then the contribution of the reaction (r) to the LHS of Eq. (2) may be calculated as

$$\Delta_{r}H_{m}d\xi_{r}/dt = \frac{I}{2F}\Delta_{r}H_{m} \tag{7}$$

b2) The gases produced by electrolysis, in an amount of 1.5 ξ_r, will be saturated with D_2O at a pressure p^*. This calls for evaporation

$$\text{(vap)} \qquad D_2O(l,T) \rightarrow D_2O(g,T,p^*) \tag{8}$$

The amount evaporated, ξ_{vap}, may be found from Dalton's law since $\xi_{vap}/(\xi_{vap} + 1.5\,\xi_r) = p^*/p$ so that $\xi_{vap} = 1.5\,\xi_r p^*/(p-p^*)$ where p is the total pressure. Hence the calculated contribution of evaporation to the LHS of Eq. (2) is

$$\Delta_{vap}H_{D_2O} \cdot d\xi_{vap}/dt = \frac{3I}{4F}\Delta_{vap}H_{D_2O}\,p^*/(p-p^*) \tag{9}$$

b3) During electrolysis some deuterium atoms or ions will become absorbed into the palladium, giving rise to a negative enthalpy contribution. There is evidence that the molar enthalpy of forming ($\alpha + \beta$) phase is about -40 kJ $\cdot(\text{mol } D_2)^{-1}$; for a survey see Ref. [3]. The total amount absorbed is slight, however, and in the steady state its increase with time will be neglected here.

The combined rate of change of enthalpy due to electrolysis and evaporation, $d\Delta H_{calc}/dT$, is obtained by adding (7) and (9):

$$d\Delta H_{calc}/dt = \frac{I}{2F}[\Delta_r H_m + 1.5\,\Delta_{vap}H_{D_2O}\,p^*/(p-p^*)] \tag{10}$$

while the observed rate of change of enthalpy is given by

$$d\Delta H_{obs}/dt = P + \Phi \tag{11}$$

Their difference gives the rate of change of enthalpy not accounted for, the excess enthalpy per unit of time $d\Delta H_{ex}/dt$:

$$\dot{H}_{ex} = d\Delta H_{ex}/dt = d\Delta H_{obs}/dt - d\Delta H_{calc}/dt. \tag{12}$$

These quantities are calculated in the next section using Tables 2 and 3 of Ref. [1], hereafter referred to as FT2 and FT3, for (11), and with independent data for (10).

Numerical values

The current I is obtained from current densities and electrode dimensions given in Table FT3. Each current found was close to one from the set {1.600 A, 0.800 A, 0.400 A, ..., 0.025 A}, and these were adopted.

For the reaction (r), JANAF thermochemical Tables 4, 5 give the following standard values at 298.15 K: $\Delta_r H_m^\theta = 294600\ \mathrm{J\cdot mol^{-1}}$, $\Delta_r C_{p,m}^\theta = (29.20 + 1/2 \times 29.36 - 84.35)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} = -40.5\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. Hence

$$\Delta_r H_m^\theta = [294600 - 40.5(T/\mathrm{K} - 298)]\ \mathrm{J\cdot mol^{-1}} \tag{13}$$

which will be applied to calculate $\Delta_r H_m(T)$ with negligible error.

For the evaporation (vap) the following values of the vapour pressure of deuterium oxide p^*, based on measurements by Kirschenbaum [6], were taken from Landolt-Börnstein [7]: $\theta/°\mathrm{C}$, p^*/Torr = {30, 28.0; 40, 49.3; 50, 83.6; 60, 136.6}. They may be approximated with sufficient accuracy by

$$l\,n(p^*/\mathrm{Pa}) = -5337\,\mathrm{K}/T + 25.83 \tag{14}$$

It follows that $\Delta_{vap}H_{D_2O} = 44370\ \mathrm{J\cdot mol^{-1}}$. The pressure of the experiment is conveniently taken to be 1 bar = 10^5 Pa.

It is now possible to calculate the combined molar enthalpy (10) for a given temperature; it ranges from 296.98 $\mathrm{kJ\cdot mol^{-1}}$ at 30°C to 308.01 $\mathrm{kJ\cdot mol^{-1}}$ at 60°C. Unfortunately, the temperature of the individual experiment is not given in FT3, but knowing Φ ($= -Q_{\mathrm{input}}$ in the heading) it may be estimated as follows. In FT2 observed values of Φ ($= -Q_{\mathrm{applied}}$ + constant contribution from electrolysis) and θ are given. Fitting a second-degree polynomium in ΔT (cf. Eq. (5)) to these values one obtains, for the given calorimeter, the expression $\Phi/W = -2.652 + 60.4\cdot 10^{-3}\ \theta/°\mathrm{C} + 934\cdot 10^{-6}\ (\theta/°\mathrm{C})^2$ which may be solved for θ when Φ is known. This was done for all experiments listed in FT3. Dissimilarities between calorimeters may produce an error of one or several K; an error of 1 K in T will give rise to errors of 0.1 $\mathrm{kJ\cdot mol^{-1}}$ at 30°C and 0.9 $\mathrm{kJ\cdot mol^{-1}}$ at 60°C in ΔH_{calo}

Finally P is found as $U\cdot I$ while Φ is identified with $-Q_{\mathrm{input}}$ in FT3 as calculated by Fleischmann *et al.*

Results

Values of cell voltage, total current, current density, cell temperature estimated from Q_{input} in FT3, electric power, heat flow into the cell, observed and calculated enthalpy rates of change and their difference $\mathrm{d}H_{\mathrm{ex}}/\mathrm{d}t = \dot{H}_{\mathrm{ex}}$ as well as the corresponding quantity Q_{excess} given by Fleischmann *et al.* are all listed in Table 1 of the present paper. For ease of reference the figures in Table 1 are given in the same vertical order as in FT3.

The agreement between $\dot{H}_{\mathrm{obs}}$ and $\dot{H}_{\mathrm{calc}}$ is seen to be quite satisfactory, as testified by their difference $\dot{H}_{\mathrm{ex}}$ which is negative and small in all cases.

Attempts were made to correlate $\dot{H}_{\mathrm{ex}}$ with the other columns of Table 1. They failed in all cases but one: when $\dot{H}_{\mathrm{ex}}$ (or its negative) is plotted against the electric power P a smooth, monotonous functional relationship emerges, as shown in Fig. 1. For comparison those Q_{excess} values which fall within its frame are added to the figure (six had to be omitted, all being >1 *W*); they are not only larger by an order of magnitude or more but also present a much larger relative scatter than those obtained here. By contrast the present data defines with fair precision a function $-\dot{H}_{\mathrm{ex}}(P)$ which is zero for $P = 0$ *W* and increases so rapidly with P that an exponential is called for.

To account for the shape of this function, recall that the cell temperature θ increases nearly linearly with P. If the excess reaction rate depends on temperature in the usual fashion, its logarithm will vary linearly with T^{-1}. This

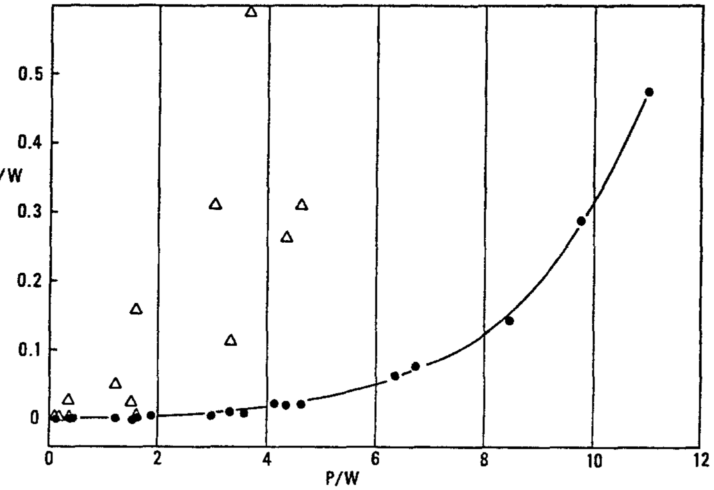

Fig. 1 Plot of the negative excess-enthalpy rate of change $-\dot{H}_{\mathrm{ex}}$ in $\mathrm{J \cdot s^{-1}}$ calculated by the present method (•), and by Fleischmann *et al.* [1] (Δ) *vs.* the electric power of electrolysis P in W. Of all the quantities in Table 1 the power is the only independent variable which gives a monotonous function. The graph may be approximated by an exponential function of P, but not by a mere power of P.

Table 1 Excess enthalpy rate of change $\dot{H}_{ex} = dH_{obs}/dt - dH_{calc}/dt$ calculated a $P + \Phi$ (power in minus heat-flow-out) minus $\Delta H_m \cdot I/2F$ computed independently from accepted enthalpy values. Same row order as Table 3 in Ref. [1]

Voltage U/V	Current I/A	Current density j/mA·cm^{-2}	Est. cell temperature θ/°C	Electric power P/W	Heat flow (negative) $-\Phi$/W	dH_{obs}/dt $= P + \Phi$ $\dot{H}_{obs}$/W	dH_{calc}/dt $\dot{H}_{calc}$/W	$-\dot{H}_{ex}$ (present) $-\dot{H}_{ex}$/W	$-\dot{H}_{ex}$ Ref. [1]) Q_{excess}/W
2.811	0.025	64	30.3	0.070	0.032	0.038	0.038	0.000	0.001
4.000	0.400	128	37.9	1.600	0.984	0.616	0.618	0.002	0.160
3.325	0.050	128	30.8	0.166	0.089	0.077	0.077	0.000	0.005
5.201	0.800	256	51.5	4.161	2.93	1.231	1.254	0.023	0.313
6.085	1.600	512	75.7	9.736	7.27	2.47	2.756	0.290	1.05
11.640	0.400	1024	58.3	4.656	4.04	0.62	0.636	0.020	1.03
4.780	0.400	64	40.3	1.912	1.30	0.61	0.619	0.007	0.006
3.930	0.400	64	37.7	1.572	0.956	0.616	0.618	0.002	0.024
8.438	0.800	128	66.6	6.750	5.52	1.23	1.306	0.076	1.65
4.044	0.100	128	32.1	0.404	0.250	0.154	0.154	0.000	0.028
6.032	0.200	256	37.3	1.206	0.898	0.308	0.309	0.001	0.056
9.042	0.400	512	51.9	3.617	3.00	0.62	0.627	0.010	0.60
7.953	0.800	1024	64.5	6.362	5.13	1.23	1.295	0.063	2.80
5.419	0.800	64	52.6	4.335	3.10	1.24	1.256	0.021	0.263
4.745	0.700	64	46.9	3.322	2.24	1.08	1.091	0.010	0.117
3.519	0.100	64	31.7	0.352	0.198	0.154	0.154	0.000	0.0005
6.852	1.600	128	81.6	10.963	8.50	2.46	2.941	0.478	1.05
7.502	0.400	256	47.9	3.001	2.38	0.62	0.624	0.003	0.311
10.580	0.800	512	75.5	8.464	7.23	1.23	1.376	0.142	1.65

is not all, however: the rate is zero when no electrolysis takes place, i.e. at $I = 0\,A$, and increases with increasing I. The simplest assumption, that $\dot{H}_{ex}$ and I are proportional, is tested in Fig. 2, in which $\ln|\dot{H}_{ex}/I\,|$ (in volts) is plotted against T^{-1}. The ten points of highest $\dot{H}_{ex}/I$ values lie remarkably close to a straight line while the remaining nine are rather scattered. This is to be expected since they all correspond to $\dot{H}_{ex}$ values close to zero.

Figure 2 supports a relationship of the form

$$\dot{H}_{ex} = -k\,I\exp(-E_a/RT) \qquad (15)$$

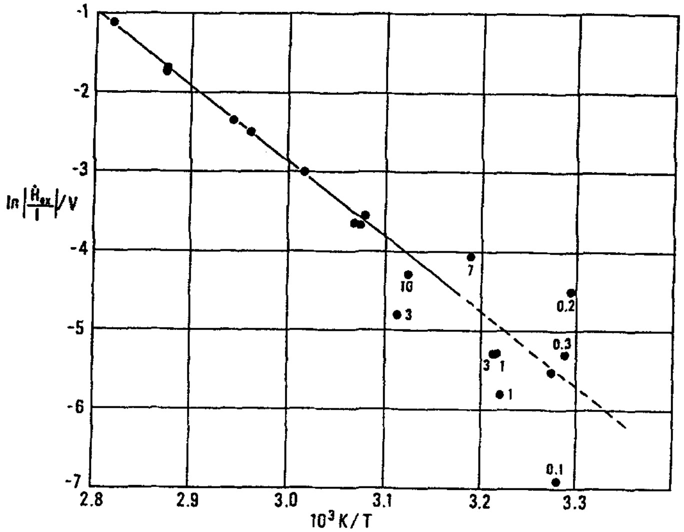

Fig. 2 Plot of the natural logarithm of the ratio $|\dot{H}_{ex}/I|$ in V *vs.* T^{-1} in K^{-1}. The relationship is close to linearity in the range $10 < -\dot{H}_{ex}$ /mW < 478; for values lower than 10 mW the relative uncertainty of $|\dot{H}_{ex}|$ becomes prohibitively large, as shown by the scatter. The figures give the values of $\dot{H}_{ex}$ /mW in this range

Disregarding the four points for which $|\dot{H}_{ex}| < 1$ mW, linear regression gives $\dot{H}_{ex}/\mathrm{W} = -1.13\cdot10^{12}\exp(-85\ \mathrm{kJ\cdot mol^{-1}}/RT)\ I/\mathrm{A}$ with a correlation coefficient of –0.97.

To demonstrate the validity of Eq. (15), consider the fifth and the last row of Table 1 which relate to experiments made at roughly the same temperature. The ratio between currents is 1.6/0.8, and between $\dot{H}_{ex}$ values 0.290/0.142. Similar evidence is found from rows 4, 14 and 12.

Discussion

The bursts found by Fleischmann and co-workers and illustrated in Figs. 8A and 8B of Ref. [1] cannot be explained by the present method. Their presence, as inferred from the temperature record, is unquestionable, but convincing evidence as to their origin is still missing.

Leaving the bursts out of account, the bulk of the data permits the following conclusions.

a) At low electrolysis current, the calculations by Fleischmann and co-workers agree with those presented here in that the excess enthalpy is zero: the calorimetric data agrees with accepted thermodynamic values.

b) At higher currents, negative excess enthalpies are found in both cases, but the Fleischmann *et al.* values are higher than those found here by one or two orders of magnitude, varying between experiments. The discrepancy could originate in their indirect statistical treatment, of which no standard deviation is given. Trials to correlate both sets of results with the experimental variables were successful in the present case only (columns 5 and 9 of Table 1; Fig. 1). They show $\dot{H}_{ex}$ to be proportional to the total current and to an Arrhenius factor with an activation enthalpy of about 85 $\text{kJ}\cdot\text{mol}^{-1}$.

c) A third outcome of the experiments should not be overlooked: they show that the (negative) increase of excess enthalpy continues over very long periods of time, 10^6 or even 10^7 seconds. At a rate of 0.1 to 0.5 $\text{J}\cdot\text{s}^{-1}$, the total enthalpy liberated adds up to the megajoule range. No chemical change of state of the calorimeter can explain this, if only because of its size.

A trivial interpretation suggests itself: some of the deuterium and oxygen formed by electrolysis might combine instead of leaving the cell, in which case the excess enthalpy would be the heat of formation of deuterium oxide, multiplied by its formation rate. This would account for all observed facts. If the statement, made by Fleischmann *et al.* (p. 301 in [1]), that current efficiencies were determined, and were higher than 99% applies to every experiment, the recombination hypothesis must, of course, be rejected; but if determinations were made in gentle conditions, with $P < 3$ W, say, recombination would hardly be perceptible. In view of its simplicity, this tentative interpretation should be tested.

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Zusammenfassung — Das von vielen Elektrochemikern verwendete Verfahren zur Berechnung der Enthalpie in kalorimetrischen Messungen an Elektrolysereaktionen wurde unter Anwendung der von Fleischmann et.al. in einer Fallstudie [J. Electroanal. Chem., 287 (1990) 293.] veröffentlichten Angaben mit einer rein thermodynamischen Näherung verglichen. Eine Reihe von mit der ersten Methode erhaltenen Überschußwerten $dH_{ex}/dt = dH_{obs}/dt - dH_{calc}/dt$ korrelierte weder mit den experimentellen Parametern noch mit den entsprechenden, thermodynamisch gefundenen Werten. Letztere, um etwa zwei Größenordnungen kleinere Werte konnten durch die Gleichung $dH_{ex}/dt = -kI \exp(-E_a/RT)$ mit einer Aktivierungsenthalpie von etwa 85 $kJ \cdot mol^{-1}$ beschrieben werden. Es wird deshalb nahegelegt, daß dies einer Rekombinierung der Elektrolysegase zugeschrieben werden kann.